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STUDIES ON POLYCYCLIC AROMATIC HYDROCARBONS IN FLAMES

Ronald Long

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Studies on Polycyclic Aromatic Hydrocarbons in Flames

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Studies on Polycyclic Aromatic Hydrocarocarbons in Flames

by

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ABSTRACT

The analytical method developed in the early stages of the work involving Soxhlet extraction of the particulate matter followed by column chromatography and then programmed-temperature gas chromatography (with the use of u. v. spectrophotometry to identify individual polycyclic aromatics) has been simplified and made more rapid.

The improved procedure has been used to analyse soot samples in later work and, inter alia, the p. c. a. h. in soot samples from three fire fighting schools in the U. S. A. The presence of appreciable amounts of known carcinogens in these suggests a possible health hazard to personnel exposed.

Exploratory work has been carried out on the use of the integrated ion-current technique in high resolution mass spectrometry to determine picogram quantities of p. c. a. h. introduced into the ion source of a GEC-AEI, M. S. 9. instrument, a low electron voltage (13ev) ensuring that only the molecular ions are formed. Such a method has been shown to be potentially valuable in air pollution studies in conjunction with thin layer chromatography, or in certain cases on its own.

Samples have been withdrawn from rich oxy-acetylene and oxy-ethylene low pressure flat flames using quartz micro-probes. These have been analysed by mass spectrometry and gas chromatography. There is a marked similarity in the flames and the concentration profiles of, inter alia, diacetylene and other polyacetylenes, phenyl acetylene and styrene and certain polycyclic aromatics have been determined. The results suggest

that acetylene plays an important intermediate rôle in the formation of p.c.a.h. The results relating to the formation of polyacetylenes confirm those of previous workers but those relating to p.c.a.h. differ in important respects. The mode of formation of the polycyclic aromatics is considered.

Although it has not proved possible to undertake that part of the programme involving the use of organo-metallic additives, contemporary research in Germany and in England has been reviewed briefly.

LIST OF PUBLICATIONS RESULTING FROM RESEARCH SUPPORTED BY GRANT AP OO323

1. Gas chromatographic analysis of polycyclic aromatic hydrocarbons in soot samples. B. B. Chakraborty and R. Long.
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   II, 217, (1968).

2. The formation of soot and polycyclic aromatic hydrocarbons in diffusion flames. B. B. Chakraborty and R. Long.

Part I.	Combustion and Flame,		12,226 (1968).
Part II.	"	"	12, 237, (1968).
Part III	"	"	12, 469, (1968).

3. The formation of soot and polycyclic aromatic hydrocarbons in ethylene diffusion flames with methanol as additive.
   B. B. Chakraborty and R. Long. Combustion and Flame. 12, 168, (1968).

4. Soot formation in ethylene and propane diffusion flames.
   P. Dearden and R. Long. J. Applied Chem. 18, 243, (1968)

5. The flux of polycyclic aromatic hydrocarbons and insoluble matter in pre-mixed acetylene - oxygen flames.
   E. E. Tompkins and R. Long. 12th Symposium (International) on Combustion. The Combustion Institute, Pittsburgh. (1969) page 625.

6. Mass spectrometic and chromatographic techniques for the determination of polycyclic compounds.
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7. The use of thin-layer chromatography and mass spectrometry for the rapid estimation of trace quantities of air pollutants. J. R. Majer, R. Perry and Miss M. J. Reade. J. Chromatog. 48, 328, (1970).

8. Detection of geometrical isomers by fractional sublimation in a mass spectrometer. J. R. Majer and R. Perry. J. Chem. Soc. (Section A) 822, (1970).

9. The use of mass spectrometry in the analysis of air pollutants. R. Perry, R. Long and J. R. Majer. Paper CP-37E. Second International Clean Air Congress, The International Union of Air Pollution Prevention Associations, Washington D.C. December 1970.

Ph D. theses (University of Birmingham)

1. P. Dearden, May 1967.
'The formation of soot during the incomplete combustion of hydrocarbons in a diffusion flame'.

2. B. B. Chakraborty, February 1967.
'Formation of polycyclic aromatic hydrocarbons during incomplete combustion of hydrocarbons in a diffusion flame.

3. E. E. Tompkins, May 1968.
'The formation of polymeric materials and polycyclic aromatic hydrocarbons in pre-mixed acetylene/oxygen flat flames.

4. B. D. Crittenden, February 1972.
'The formation of polycyclic aromatic hydrocarbons in rich pre-mixed oxy-acetylene and oxy-ethylene flames.'

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In the preparation of Part IV of this report, the writer has drawn heavily from the Ph.D. thesis of his former research student B.D. Crittenden.

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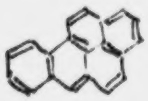
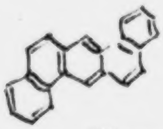
STUDIES ON POLYCYCLIC AROMATIC HYDROCARBONS IN FLAMES

INTRODUCTION

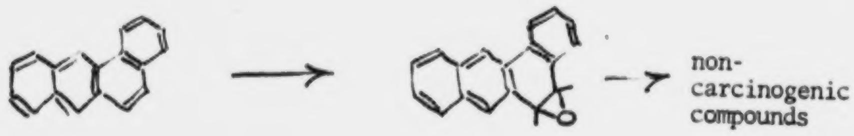
It has been known for many years that benzo (a) pyrene is a potent carcinogen and that some other polycyclic aromatic hydrocarbons e.g. dibenz (a,h) anthracene are also carcinogenic.


benzo (a) pyrene


dibenz (a, h) anthracene

The livers of many animals are able to metabolise a wide range of molecules and it has recently been shown that some polycyclic aromatic hydrocarbons can be converted initially to epoxides, which can be detected as products of metabolism, although further metabolism gives either the diol or derivatives.

Thus, in the case of benz (a) anthracene, the 5. 6- epoxide can be formed which is extremely carcinogenic and mutagenic, although benz (a) anthracene itself is only regarded as being weakly carcinogenic.



benzo(a) anthracene

5. 6 - epoxide
(carcinogenic)

Polycyclic aromatic hydrocarbons are well-known to be associated with soot or particulate carbonaceous matter resulting from the incomplete combustion of fossil fuels. Whilst cigarette smoking is a most important causal factor in lung cancer there might well be an air pollution factor too, since the frequency of the disease is higher in urban that in rural areas.

pollutants must also be recognized.

A considerable amount of work has been carried out by G. M. Badger and his associates on the mode of formation of benzo(a) pyrene and other polycyclic aromatic hydrocarbons during hydrocarbon pyrolysis but comparatively little has been published on the mode of formation of polycyclic aromatics during incomplete combustion in flames.

The objectives of the present research were as follows: -

1. To develop appropriate analytical methods for polycyclic aromatic hydrocarbons in soots and particulates and in particular to study methods employing gas chromatography and mass spectrometry.

2. To study the formation of these compounds in both pre-mixed and diffusion flames of simple hydrocarbons and the factors influencing this. In particular, stable compounds likely to suggest the mode of formation of polycyclic aromatics were to be sought.

3. To seek organo-metallic additives which might lead to a reduction in the formation of p. c. a. h. since pyrolysis and oxidation processes can often be influenced by catalysts and additives.

This report comprises five parts; Part IV is the more detailed one as our publications and progress reports have already dealt with the earlier work in some detail, and consequently it is not considered worthwhile reporting this again here. Part V is a brief review of the work of others since, unfortunately, the loss of key personnel precluded work in this area.

Part I:- deals with improvements made in the gas chromatographic method of analysis of polycyclic aromatic hydrocarbons in soots since the description of the earlier work by B. B. Chakraborty and R. Long. The use of a solvent of low boiling point (and toxicity)*, rotary evaporation under vacuum at a low temperature, the discarding of the initial separation by column chromatography, the use of an internal standard in the gas chromatography and of high resolution mass spectrometry in the identification of individual p. c. a. h., have all been improvements.

Part II:- applies the above method to the analysis of soots collected from fire-fighting schools in the U. S. A. These soots are shown to contain appreciable amounts of known carcinogens and consequently exposure to the smoke may well constitute a health hazard to personnel.

Part III:- describes an offshoot of the present work viz. the application of the integrated ion-current technique in mass spectrometry to the resolution of isomeric compounds not readily separable by gas chromatography. Thus, benzo (a) pyrene might be estimated in the presence of benzo (e) pyrene and perylene. In conjunction with other techniques of separation such as gas chromatography or thin layer chromatography this method seems to offer potential. The combination of T. L. C. with high resolution mass spectrometry results in a highly sensitive and rapid method of analysis for polycyclic aromatic hydrocarbons.

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* Compared with benzene or chloroform

Part IV:- the main section, describes work carried out with the aim of finding out more about the mode of formation of polycyclic aromatic hydrocarbons during incomplete combustion in flames. The earlier work already published by P. Dearden and R. Long and by B. B. Chakraborty and R. Long respectively, is not considered here; attention being paid to as yet unpublished work. A relatively quick and reliable method has been devised for withdrawing samples, at different heights above the burner, from rich oxy-acetylene and oxy-ethylene low pressure flat pre-mixed flames. High resolution mass spectrometry has been used for the analysis of more volatile species and programmed - temperature gas chromatography has been used for the analysis of less volatile species including polycylic aromatic hydrocarbons. Both u. v. absorption spectroscopy and mass spectrometry have been used to identify species in the latter case. The results show that, in general, the same products are formed in rich oxy-acetylene and oxy-ethylene pre-mixed flames, suggesting that the polycyclic aromatic are formed by the same route in each case. The results confirm the important rôle of acetylene in hydrocarbon flames and in particular the results are in general agreement with the pioneering work of K. H. Homann and H. Gg. Wagner who found that polyacetylenes reach a maximum concentration at the end of the oxidation zone and that soot formation begins at the zone where the polyacetylene concentration falls off. The present work supports a scheme of G. M. Badger for polycyclic aromatic formation during pyrolysis in that certain compounds with a two carbon atom side-chain attached to a benzene ring appear to represent "key" aromatic species formed from acetylene, although the reactions involved are likely to involve free radical, rather than molecular species. Such substances believed to be important as precursors of polycyclic aromatics include phenylacetylene and styrene. The experimental evidence does not favour ethylene or 1.3 butadiene as important intermediates. Although only stable species can be sampled, these are considered to give useful information as to likely steps involved in the formation of the polycyclic aromatic hydrocarbons in flames.

Part V:- While the effect of introducing oxygen into the combustion air, or to the hydrocarbon itself, in a diffusion flame has been reported earlier, no progress has been made in examining the effects of organo-metallic additives, owing to loss of key personnel at certain stages of the work. However, recent work in Germany by G. Spengler and G. Haupt has indicated that reduction in soot and polycyclic aromatic hydrocarbons by this means is feasible and work on the suppression of soot and p.c.a.h. in flames by the use of metal additives has recently been published. D. H. Cotton, N. J. Friswell and D. R. Jenkins claim that the mechanism of action of the alkaline earth metals is one of gas-phase catalysis of the decomposition of hydrogen or water vapour giving rise to the formation of hydroxyl radicals which remove soot or precursors of soot.

Part I Improvements in the Gas Chromatographic Analysis of Polycyclic Aromatic Hydrocarbons in Soot Samples.

The gas chromatographic method described by B. B. Chakraborty and Ronald Long (Environmental Science and Technology, I, 828-834, (1967) has been improved and made more rapid in the following way

i) The use of methylene chloride (in place of chloroform) as solvent in the extraction process enables this to be carried out at a temperature below 40°C and so helps to prevent the possibility of any further reaction in the Soxhlet apparatus.

ii) This solvent is readily removed from the extracted polycyclic aromatics by rotary evaporation under vacuo at 0°C thus avoiding loss of more volatile hydrocarbons. (Such as benzene, phenylacetylene, naphthalene).

iii) The initial separation by column chromatography does not seem to be necessary and the analysis is thus speeded up considerably by direct injection of an extract of soot into the G. C. column.

Thus, a Soxhlet extraction of 0.5 g. of soot is carried out for six hours using 250 ml of methylene chloride as solvent. The resultant solution is evaporated down under vacuum at 0°C and the residue is dissolved in 2 ml. of methylene chloride. 25 μl. of this solution are used for the programmed temperature gas chromatography as described previously.

iv) The use of 3 methyl phenanthrene as internal standard increases accuracy and also aids in the preliminary identification of components by retention time ratios.

v) High resolution mass spectrometry is used in identifying the component(s) of certain gas chromatographic peaks. (ef. Part IV)

The above method has been used in Part II

PART II Gas Chromatographic Analysis of Polycyclic Aromatic Hydrocarbons in Soot Samples from Firefighting Schools in the U. S. A.

Peak No. in Gas Chromatogram	Compound	Quantities in mg per gram soot. City A (Norfolk)	City B (San Francisco)	City C (Philadelphia)
1	Naphthalene	0.15	0.6	0.15
2	Acenaphthylene	0.05	0.4	0.15
3	Fluorene	0.05	0.4	0.8
4	Phananthrene/ Anthracene	0.4	2.4	2.2
5*	Methyl phenanthrenes	0.4	3.0	4.3
6*	4,5 - Methylene phenanthrene	0.15	1.8	1.7
7	Fluoranthenes	0.3	4.6	6.1
8	Pyrene	0.6	7.8	8.6
9	Benzofluorenes	0.1	1.2	1.5
10	Methyl pyrenes	0.05	1.0	0.15
11	Benzo (m, n, o) fluoranthene	0.2	2.0	2.0
12	Benzoanthracene/ Chrysene	0.4	4.6	2.0
13	Benzo fluoranthenes	0.5	3.5	1.3
14	Benzo(a)pyrene Benzo(e)pyrene and Perylene**	0.9	4.5	1.2
15	Indeno (1, 2, 3-c, d) pyrene	0.4	3.3	none detected
16	Benzo (g, h, i) perylene	0.4	2.5	"
17	Anthanthrene	0.05	0.9	"

* identified by reference to earlier work.

** mass spectrometric measurements indicate about 50% benzo (a) pyrene.

(We are indebted to Dr. A. R. Siedle (U.S. Navy Preventive Medicine Unit, 2, Norfolk, Va for the samples, provided at his initiative).

Part III. The Integrated Ion-Current Technique in Mass Spectrometry.

In conventional quantitative mass spectrometry, calibration of the instrument is carried out for a specific compound by maintaining a reservoir of the vapour of this compound at constant pressure whilst allowing the compound to leak from the reservoir into the ion source of the mass spectrometer at a very slow rate. The sensitivity of the instrument may then be expressed in terms of the ion current measured at any selected m/e value for a given partial pressure of the compound in the inlet reservoir. Such a method is quite unsuitable for the examination of samples of relatively involatile solid materials. It is then more appropriate to evaporate completely a small weighed sample of the solid material and to record the ion-current at a selected m/e value during the course of this evaporation. The sensitivity of the instrument may then be expressed in terms of the integrated ion-current obtained at the selected m/e value for a given weight of sample evaporated.

When a voltage scanning or quadrupole mass spectrometer is being used, it may be possible to tune into the appropriate mass before the ion-current at that m/e value is established. This is not so simple when a magnetic scanning instrument is used and it may be necessary to use a calibrating substance, usually the vapour of heptacosa fluoro tri-n-butyl amine to calibrate the mass scale. The peak switching facilities of the instrument can then be used to tune into the required mass before evaporation begins and the effects of any slight instrumental drift are obviated. The record obtained consists of a series of peaks drawn at one second intervals, the height of which correspond to the instantaneous ion-current. It is the envelope of this

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record which is proportional to the integrated ion-current and hence to the amount of sample evaporated.

When the sample consists of two substances the mass spectra of which both contain a peak at a specific m/e value the integrated ion-current may show fine structure because the rates of evaporation of the two compounds may be different. This effect is most marked when recording the molecule ion-current of a substance which can exist in two isomeric forms.

Using a GEC -AEI, MS9, mass spectrometer J. R. Majer and R. Perry[i] have shown that by the above technique anthracene and phenanthrene can be clearly separated. Benzo (a) pyrene is found in products of incomplete combustion along with two comparatively non-carcinogenic isomers, benzo (e) pyrene and perylene. By the above technique benzo (a) pyrene can be separated either from perylene or from benzo (e) pyrene, although benzo (e) pyrene cannot be separated from perylene.

Synthetic mixtures of polycylic aromatic hydrocarbons have been separated by thin layer chromatography for subsequent determination in the above manner by J. R. Majer, R. Perry and M. J. Reade.[ii] Calibration curves were constructed using standard solutions of each compound and these were linear in all ranges between 10^{-6} and 10^{-12} g.

Provided the position of the eluted spot sample is known., these authors claim that it is possible to transfer samples in the picogram range from the chromatogram to the mass spectrometer. Extraction of the polycyclic aromatic from the cellulose adsorbent can be carried out in a micro centifuge tube with as little as 20μl of solvent, enabling a large part of the eluted sample to be used in the mass spectral assay.

R. Perry, R. Long and J. R. Majer[iii] have published a paper indicating the sensitivity and versatility of the integrated ion-current technique with polycyclic aromatics by comparing the analysis of a soot extract obtained by mass spectromety with that obtained by gas chromatography. For gas chromatography the concentration of the solution used was a hundred times that used for mass spectrometry and a 25 µl aliquot was used compared to a 5 µl aliquot used in the integrated ion-current method.

The usefulness of the mass spectrometer as a qualitative instrument for the identification of polycyclic aromatic hydrocarbons in soot samples has been demonstrated by M. Chaigneau, L. Giry and L.-P. Ricard[iv] who have shown that 75 compounds can be identified in soots, including 34 hydrocarbons many of which are polycyclic aromatics. The above mentioned quantitative technique, however, seems to offer some potential in the field of air pollution studies.

References - Part III

i) J. R. Majer and R. Perry. J. Chem. Soc. (Sect. A) 822(1970)

ii) J. R Majer, R. Perry and Miss M. J. Reade.
J. Chromatog, 48 328 (1970)

iii) R. Perry, R. Long and J. R. Majer. Paper CP-37E. Second Internat. Clean Air Congress. Washington D. C. Dec. 1970

iv) M. Chaigneau, L. Giry and L-P. Ricard
Chimie Analytique 51, 187, (1969)

Part IV The Mode of Formation of Polycyclic Aromatic Hydrocarbons in Rich Pre-Mixed Flat Flames

(This section of the Report is based on the Ph. D. thesis of B. D. Crittenden, without appreciable alteration. It is proposed to publish a paper on these results at a later date - the conclusions drawn in the paper might well be slightly different from those reported here when the results have been re-examined critically).

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1.1 Rich Premixed Flat Flames

1.1.1 Premixed and Diffusion Flames

Gaydon and Wolfhard[21] have stated that no flame may be characterised as being either purely premixed or purely diffusional in nature. For example, rich premixed Bunsen-type flames depend on the outer diffusion flame zone for their stability and diffusion flames depend on a premixing region near the burner rim for their stability[22]. Reducing the pressure of a diffusion flame increases the premixing region at its base and at sufficiently low pressures, such a flame may be indistinguishable from one of a premixed nature. The similarity between premixed and diffusion flames is more apparent in the multiple diffusion burner of the type used by Berl and Wilson[23]; as the tube spacing is reduced the array of tiny diffusion flames becomes indistinguishable from a premixed flame.

1.1.2 The Flat Premixed Flame

The requirements for such a flat flame are:

(a) that the gases entering the burner should be perfectly mixed and should leave the burner port with a perfectly uniform velocity distribution, and

(b) that the flow of gases leaving the burner port should remain undisturbed by the behaviour of the hot products.

If these two requirements are satisfied and if the velocity of the gas mixture leaving the burner port is equal to the burning velocity of the gas mixture, the flame is perfectly flat and does not require stabilisation.

Powling[24] in his studies of the accurate measurement of low burning velocities first designed a burner which would stabilise such flames. Flat flames of faster burning mixtures may be stabilised over cooled porous plate burners of the type used by Botha and Spalding[25], Kydd[26], Homann and co-workers[27,28], Yumlu[29], and Tompkins and Long[2]. In such burner systems, heat is transferred to the cooled burner plate as the flame approaches it. The temperature of the burner is little affected if it is efficiently cooled although the temperature of the gases in contact with it is considerably reduced. Thus the flame speed is reduced and as a result, the flame rapidly and automatically takes up a position of equilibrium a short distance away from the burner plate where it loses just enough heat to reduce the flame speed to that of the gas stream.

The thickness of the reaction zone in premixed flat flames depends on both the pressure and the burning velocity. Fristrom and Westenberg[30] present the following empirical relationship for an estimation of the flame front thickness (L) for fuels burning in oxygen or air.

$$L = \frac{2.5}{PV_o}$$

where L = the flame front thickness, cm.

P = the pressure, atmospheres

V_o = the flame speed, cm/sec

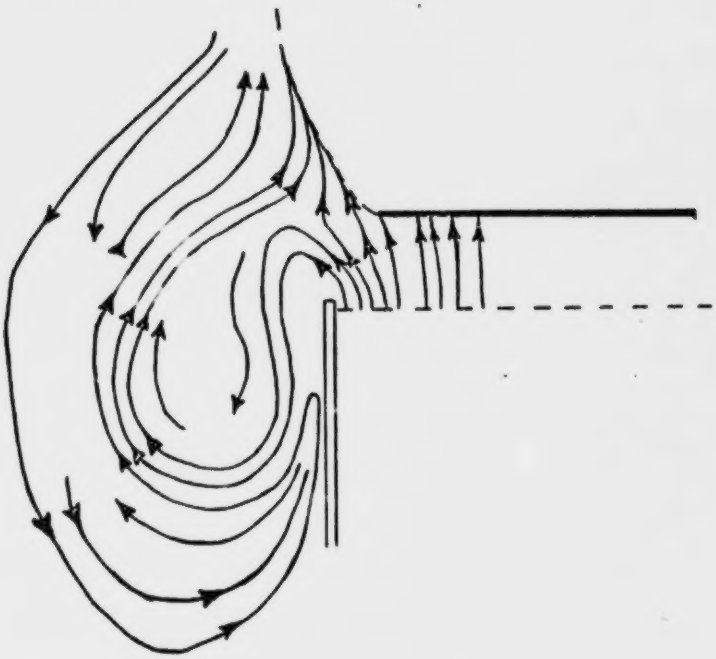
If it is assumed that the flame speed is a constant then the flame front thickness is inversely proportional to the pressure. Consequently, reducing the pressure of a rich premixed flat flame extends the reaction zone to allow measurement of concentration profiles etc., at discrete positions within it[27,28].

1.1.3 The Pseudo-one-dimensional Flame

The results of particle track studies[31] demonstrate that in practice flat flames are not truly one-dimensional and that the flame is stabilised on the burner by a toroidal vortex of gases (see Figure 1.1). Levy and Weinberg[31] have shown that the stability of the flame is diminished when (a) a column of inert gas flows upwards around the burner and (b) too narrow a chimney is used.

However, Fristrom, Grunfelder and Favin[32] have concluded that a low pressure, lean premixed oxy-methane flame is sufficiently one-dimensional to allow quantitative determination of flow velocities, mole fractions and temperatures. Fenimore, Jones and Moore[33] have shown also that samples withdrawn through critical flow quartz probes give the same O:C:H ratios at various radial positions close to the burner surface in rich premixed flat hydrocarbon flames. Singer and Grumer[34] have demonstrated that rich propane/air flat flames are one-dimensional close above the blue reaction zone but become progressively less so higher in the burned gases. This is because as the burned gases rise, they become cooler and the flame cross-sectional area decreases; consequently, edge effects become more pronounced and radial diffusion may account for poor flatness. Bonne and Wagner[28] have also shown that rich premixed flat flames are poorly one-dimensional with respect to carbon formation high in the burned gases of the flame.

Owing to the above-mentioned change in flame geometry and also to the expansion of the gases leaving the burner port (Figure 1.1) there is some difficulty in defining a flame diameter and consequently a flame cross-sectional area. The effective diameter of a flat flame burning on a



IV. Figure 1.1 Flow Pattern at the Edge of a Flat Flame Burner

(reproduced from Reference 3)

circular burner may be defined in one of three ways:

(i) as the diameter of the flat region alone

(ii) as the diameter of the flat region + $(2)^{\frac{1}{2}}$ x the base projection of the upturned edge

(iii) as the diameter of the whole flame projected onto a horizontal plane.

In this study, the cross-sectional area of the flame, A_h, at a height h cms above the burner surface is that area derived from the equation:

$$A_h = \frac{\pi}{4} \times d_h^2$$

where d_h is the optically measured diameter of the flame at a height h cms above the burner surface.

1.1.4 Reaction Products in Rich Premixed oxy-acetylene and oxy-ethylene flames

Bonne and co-workers[35] and later Tompkins[36] have found that there are three distinct zones in rich premixed oxy-acetylene and oxy-ethylene flames, namely,

(a) the non-luminous zone directly above the burner surface, which is sometimes called the preheat zone

(b) the blue-green reaction or oxidation* zone

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* In premixed oxy-acetylene and oxy-ethylene flames, Bonne, Homann and Wagner[35] have found that the region between the blue and yellow zones coincides well with the zone where the oxygen is nearly totally consumed.

(c) the yellow-orange zone of the hot burned gases.

These workers have found also that there is no separation of the blue and yellow zones as is reported by Millikan[37], Street and Thomas[38], and Fenimore, Jones and Moore[33] who have worked with premixed flames of fuel/air mixtures.

By means of a combined mass spectrometer and molecular beam sampling system, Homann and co-workers[39] have been able to detect many hydrocarbons present in the flame gases. Since the wall influence on the particles reaching the ion source of the mass spectrometer via such a sampling system is very low Bonne, Homann and Wagner[35] were able also to detect some free-radicals. In more recent work[1] Homann and Wagner have classified three groups of hydrocarbons which are found to be products in these flames:

Group 1 : acetylene and polyacetylenes with mass numbers ranging from 26 to 146

Group 2 : polycyclic aromatic hydrocarbons (pcah) with mass numbers ranging from 78 to approximately 300

Group 3 : reactive pcah with side chains and containing more hydrogen than purely polycyclic aromatic hydrocarbons (mass numbers ranging from 150 to greater than 550).

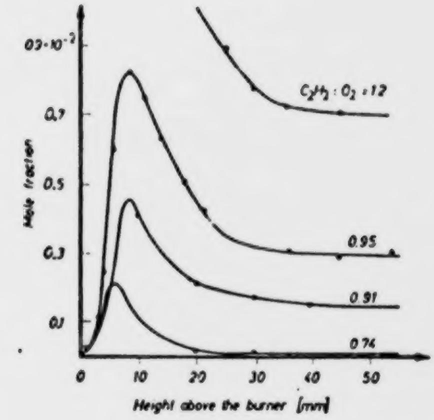
In sufficiently rich oxy-acetylene and oxy-ethylene flames, unsaturated hydrocarbons with the generic formular $C_{2n}H_2$ have been identified[35], with values of n ranging from unity (i.e. acetylene) to six (i.e. hexa-acetylene). By withdrawing samples at various heights in such flames Bonne et al[35] have shown that the concentrations of these compounds increase with increasing fuel/oxygen ratios (Figures 1.2 (a) and 1.2 (b)). Whilst the polyacetylenes are formed late in the blue (or oxidation) zone it appears that in an oxy-ethylene flame, their formation is preceded by that of acetylene[39]. The concentrations of acetylene and the individual polyacetylenes reach maximum values at the end of the blue reaction zone and then decrease to a final, roughly constant value in the burned gases (Figures 1.3 (c) and 1.4 (b)). The maximum concentrations of the polyacetylenes as well as their concentrations in the burned gases increase with increasing fuel/oxygen ratios[35] but the ratio of the maximum concentrations to final concentrations decreases. (It should be noted at this stage that increasing the fuel/oxygen ratio decreases the temperature at corresponding points in such flames[27,36].) The ratio of maximum concentration to final concentration of individual polyacetylenes becomes greater with an increasing carbon content of the polyacetylene (Figures 1.3 (c) and 1.4 (b)).

From the measured acetylene, polyacetylene and hydrogen concentrations in the flames considered, Bonne et al[35] were able to show that relationships exist between these molecules in the form of equilibria. "Equilibrium constants" were calculated for reactions such as

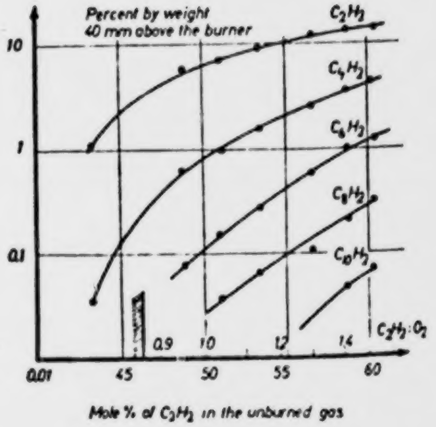
$$2C_2H_2 \rightleftharpoons C_4H_2 + H_2$$

where the "equilibrium constant", K, is given by

$$K = \frac{[C_4H_2] \times [H_2]}{[C_2H_2]^2}$$

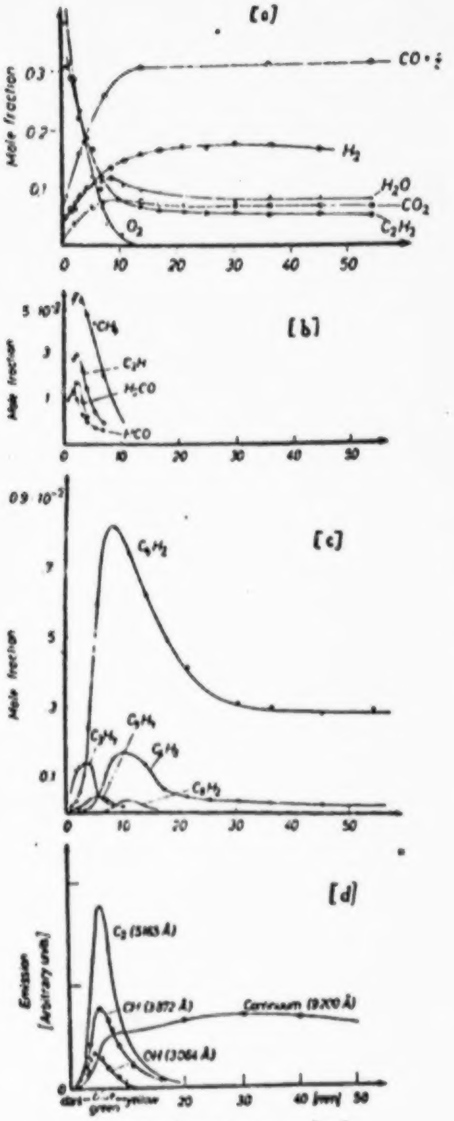


IV.**Figure 1.2 (a)** Concentration profiles of diacetylene in flat acetylene-oxygen flames of different $C_2H_2:O_2$ ratios. (p = 20 mm.Hg; flow velocity, 50 cm. sec^{-1})



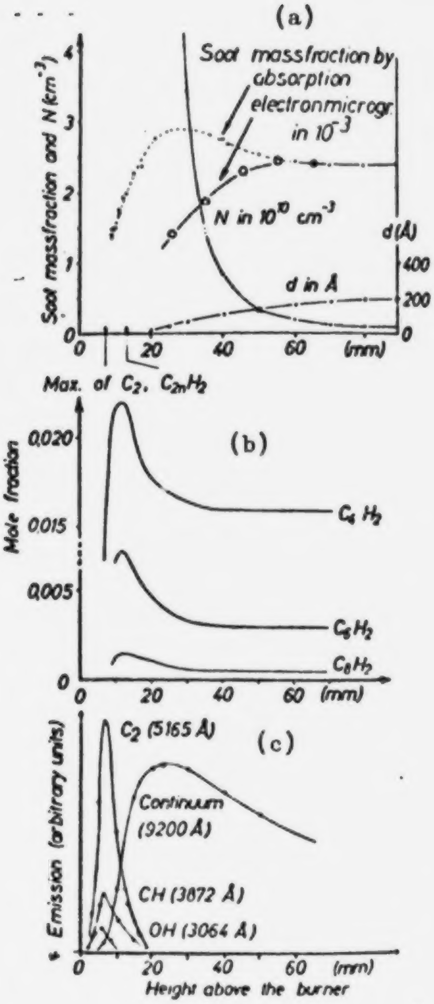
IV.**Figure 1.2 (b)** Concentration of acetylene and polyacetylenes in the burned gas of rich acetylene-oxygen flames as function of the initial $C_2H_2:O_2$ ratios. The hatched line indicates the range in which the yellow luminosity becomes visible

(reproduced from Reference 35)



IV. Figure 1.3 (a)–(c) Concentration profiles in a flat acetylene–oxygen flame ($C_2H_2:O_2 = 0.95$) at a pressure of 20 mm Hg and a flow velocity of the unburned gas of 50 cm sec^{-1}. The figure does not include all of the components which could be measured. (d) Emission of C_2, CH, and OH, and continuous emission in the same flame as function of the height above the burner.

(reproduced from Reference 35)



IV. Figure 1.4 (a) Absolute concentration of carbon, the mean number of particles and their mean diameter in a C_2H_2-O_2 flame ($C_2H_2:O_2 = 1.4$; p = 20 mm.Hg.; flow velocity, 50 cm. sec^{-1}). (b) Concentration profiles of polyacetylenes (C_4H_2, C_6H_2, C_8H_2) in the same flame (c) Emission of C_2, CH, OH and continuous emission profiles in the same flame.

(reproduced from Reference 35)

Using these "equilibrium constants", these workers have calculated the enthalpies of formation of C_4H_2 (diacetylene) and C_6H_2 (tri-acetylene) from their elements to be 109 ± 0.7 kcal/mole and 163 ± 1.2 kcal/mole, respectively.

In the discussion of their results Bonne, Homann and Wagner[35] emphasise the possible importance of polyacetylenes in the formation of 'carbon' in rich premixed flames. They have claimed that in the zone where the 'carbon' particles grow, there are no other hydrocarbons present in concentrations large enough to account for the 'carbon' which appears in the soot. (See Figures 1.4 (a)-(c)). This view is supported by the fact that increasing the fuel/oxygen ratio tends to increase the individual polyacetylene concentrations, the number of 'carbon' particles and the amount of 'carbon' produced[35].

In premixed flat oxy-acetylene flames the acetylene concentration does not fall to zero but beyond the blue zone maintains a steady value (Figure 1.3 (a)) whilst in premixed flat oxy-ethylene flames the ethylene concentration reaches zero at the end of the blue zone[39].

Other low molecular weight hydrocarbons found in these flames include propylene and methyl acetylene which reach their maximum concentrations within the oxidation zone and are destroyed before all the oxygen is consumed. The same is true for dimethylacetylene and vinylacetylene, the maximum concentrations of which precede that of diacetylene in the ethylene flame; the regions of maximum concentration of vinylacetylene and diacetylene coincide in the acetylene flame.

The results of Bonne, Homann and Wagner[35] show that there is a smooth transition between non-soot-forming and soot-forming flames as is indicated by the concentration profiles of the polyacetylenes and free-radicals and by the emission and absorption profiles of the 'carbon' particles.

In the range of fuel/oxygen ratios 0.6 to 1.2, the maximum concentration of $\dot{O}H$ radicals is reduced from 2 x 10^{-4} mole fractions by one order of magnitude[35]. It seems likely that free radicals play an important part in the oxidation reactions since radicals such as $C_2\dot{H}$, $\dot{C}H$, $\dot{O}$, $H_2\dot{C}O$ and $H\dot{C}O$ disappear rapidly at the end of the blue zone (Figure 1.3 (b)). Their disappearance is explained by the formation of heavier radicals which either cannot be detected in the burned gases or are adsorbed onto the surface of 'carbon' particles. In fact, electron spin resonance studies have shown that soot particles have many unpaired electrons, presumably because they contain free-radicals[40].

In Millikan's experiments with premixed ethylene/air flames[37] infra-red emission profiles show that acetylene is produced in the blue zone well before soot luminosity occurs and that its concentration in the burned gas remains constant, in agreement with the results of Homann et al.

Millikan found also that just downstream of the oxidation zone, the $\dot{O}H$ concentration is about eight times its equilibrium value. Since its concentration was also found to be 10^4 times that of the $\dot{O}$ radical it seems likely that the $\dot{O}H$ radical is responsible for the oxidation reactions and that it may account for the dark space which he observed between the blue and the yellow zones (see page 6).

Fenimore and Jones[41] have studied fuel-rich acetylene/oxygen flames to find that the rate of decay of acetylene in an oxygen containing atmosphere at temperatures between 1427°C and 1727°C may be represented by:

$$-\frac{d}{dt}[C_2H_2] = 2 \times 10^{12}[\dot{C}H][C_2H_2] \text{ moles/cm}^3\text{/sec}$$

These workers have also noted that the term $[\dot{C}H]$ may not be replaced by $[\dot{H}]$, $[\dot{O}]$ or $[O_2]$.

Recently Cotton, Friswell and Jenkins[42] have confirmed that alkaline earth metals reduce soot formation in a propane diffusion flame and have suggested that the mode of action of barium, calcium or strontium is the gas-phase catalysis of the decomposition of hydrogen or water vapour to produce $\dot{C}H$ radicals. In premixed flames where radical concentrations are greater than equilibrium, catalysis will tend to reduce concentrations towards equilibrium values.

In order to establish the concentration profiles of hydrocarbons in Group 2 and Group 3, Bonne, Homann and Wagner[1,43] sampled for 'carbon' particles both by condensation on thin cooled capillaries and by collection through a quartz probe connected to a mass spectrometer. The 'carbon' thus collected was heated in the ion source of a mass spectrometer. These workers found that there is always a certain amount of hydrogen associated with the 'carbon' collected at all heights in the flame, the H/C ratio being approximately unity just beyond the blue reaction zone. When the 'carbon' is heated in a vacuum, the residue is found to be practically pure carbon, indicating that all the hydrogen is bonded to relatively small volatile compounds.

The mass spectra which result from heating the 'carbon' collected from heights well into the yellow zone of the flame show major peaks at mass numbers which correspond to those of the polycyclic aromatic hydrocarbons of Group 2; the mass spectra which result from heating the 'carbon' collected just beyond the blue zone show the presence of a larger number of hydrocarbons with mass numbers ranging from 150 to 500, corresponding the the hydrocarbons of Group 3. It was suggested[1] that these latter hydrocarbons are polycyclic aromatic hydrocarbons with side chains and which are more hydrogenated than the parent pcah.

The concentration profiles of hydrocarbons of Group 2 are very similar and Homann and Wagner[1] stated that their respective concentrations steadily increase in the burned gases. They are formed later than the polyacetylenes and their individual concentrations lie on average between that of $C_{10}H_2$ and $C_{12}H_2$ with a total concentration of about 10^{-2} mole per cent of the burned gases. Since the concentration of each pcah of Group 2 increases without going through a maximum value, Homann and Wagner[1] have concluded that these pcah are not important intermediates or 'nuclei' for 'carbon' formation in an acetylene flame.

Homann and Wagner[1] could not accurately establish the concentration profiles of the hydrocarbons in Group 3 but they were able to show that they do not survive in the hot gas behind the oxidation zone. Unfortunately, they could not also identify individual compounds in this group which are present in individual concentrations of 10^{-7} mole fractions. However, since they are destroyed just beyond the blue zone they considered that the hydrocarbons of Group 3 are intermediates or 'nuclei' for 'carbon' particles.

Homann and Wagner[1] have proposed the reaction scheme outlined in Figure 1.5 for the formation of polyacetylenes and 'carbon' from acetylene and free-radicals. During the formation of the large polyacetylene molecules, the average size of the radicals involved increases. They have suggested that such large radicals might react with each other or with higher polyacetylenes to form 'aggregates', possibly involving ring closures, to produce the hydrocarbons of Group 3, since the maximum concentration of hydrocarbons in this group lies in a region where the concentration of the polyacetylenes is decreasing and the formation of pcah of Group 2 and 'carbon' is just beginning. The reactive hydrocarbons of Group 3 are probably still free-radical in nature and Homann and Wagner[1] have suggested that they might grow to small 'carbon' particles by further addition of polyacetylenes. This view is supported by the fact that the hydrogen content of the soot decreases whilst the particles are still growing.

Tompkins and Long[2] have collected 'carbon' at various heights in rich premixed oxy-acetylene flames similar to those employed by Homann and co-workers[27,28] by withdrawing samples isokinetically through a relatively large water-cooled funnel. The total collected material was extracted with chloroform for subsequent separation and identification by gas-liquid chromatography and ultra-violet spectroscopy.

The flux* profiles of the following are presented as functions of the sampling height in the flame

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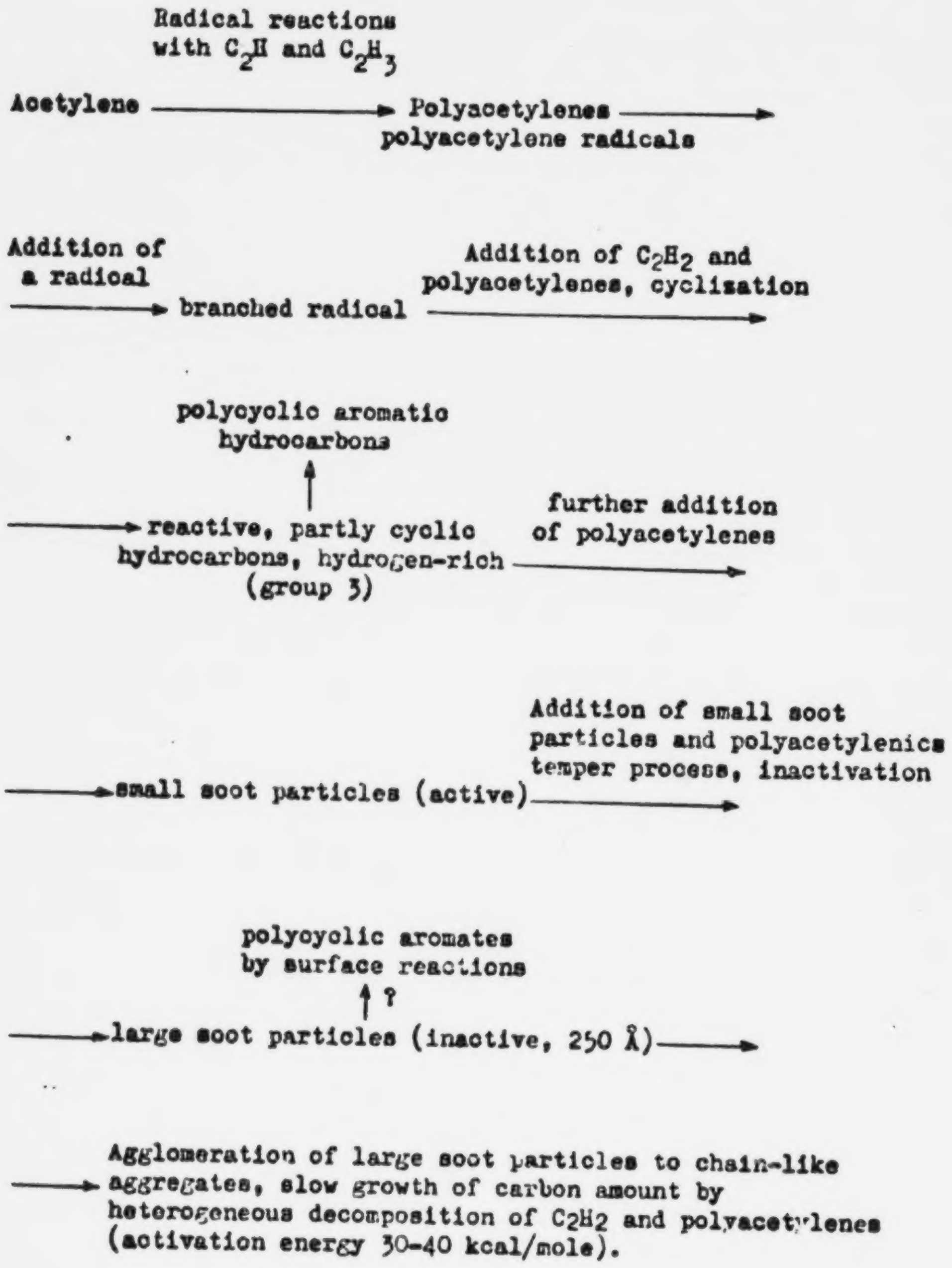
* In flames where very high concentration gradients exist, flux profiles may be very different from concentration profiles, as is explained in Appendix II.


Radical reactions with C_2H and C_2H_3
Acetylene
Polyacetylenes polyacetylene radicals
Addition of a radical
branched radical
Addition of C_2H_2 and polyacetylenes, cyclization
polycyclic aromatic hydrocarbons
reactive, partly cyclic hydrocarbons, hydrogen-rich (group 3)
further addition of polyacetylenes
Addition of small soot particles and polyacetylenics temper process, inactivation
small soot particles (active)
polycyclic aromates by surface reactions
?
large soot particles (inactive, 250 Å)
Agglomeration of large soot particles to chain-like aggregates, slow growth of carbon amount by heterogeneous decomposition of C_2H_2 and polyacetylenes (activation energy 30-40 kcal/mole).

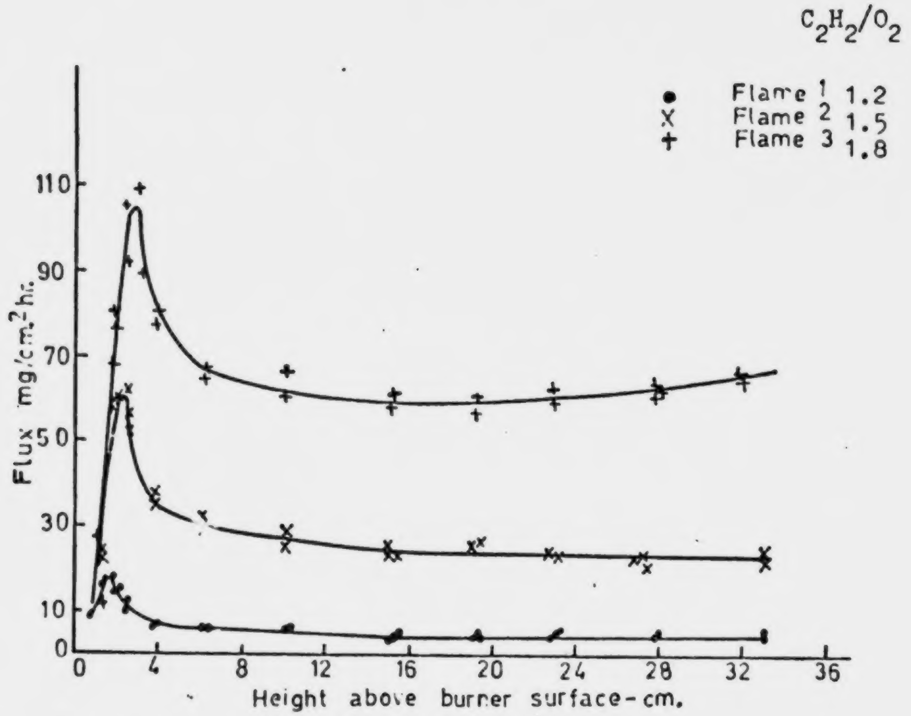
IV. **Figure 1.5** Reaction Scheme Proposed by Homann and Wagner[1] for the Formation of Polyacetylenes and 'Carbon' from Acetylene and Free-radicals

1. total collected material (Figure 1.6)
2. chloroform soluble material (Figure 1.7)
3. chloroform insoluble material (Figure 1.8)
4. total pcah (Figure 1.9)

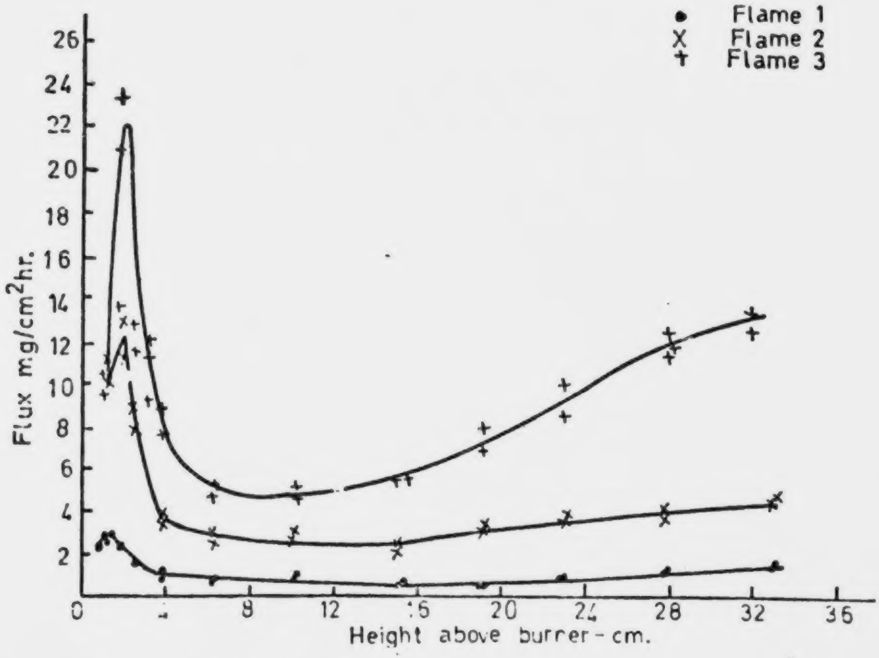
All these flux profiles reach maximum values just beyond the blue oxidation zone after the maximum temperature has been reached (Figure 1.10). Noneof the fluxes decreases to zero but each reaches a roughly constant value until a height of about 16.0 cm. in the flame when the fluxes of soluble material and pcah increase again. The fluxes of all the above materials increase with increasing fuel/oxygen ratios (Figures 1.6 to 1.9).

Table 1.1 shows the range of pcah identified by Tompkins and Long[2] in soots sampled from rich premixed oxy-acetylene flames. From their results it is apparent that there are two distinct regions of pcah formation in the flame. The first occurs near the end of the blue zone where the temperature is rapidly rising and where the acetylene and oxygen concentrations are falling[35]. Just beyond this region the pcah are destroyed, in disagreement with Homann and Wagner[1] who have stated that the concentrations of these species increase rapidly behind the oxidation zone without going through any maxima. The second region of pcah formation occurs much higher in the flame where it is suggested[2] that they might be formed by pyrolysis of residual acetylene. It is worth noting that the temperatures within this region (900° - 650°C) are those favourable for pcah formation[44].

The decline in the flux of pcah after the initial concentration maximum appears to agree with the decline in the concentration of Group 3

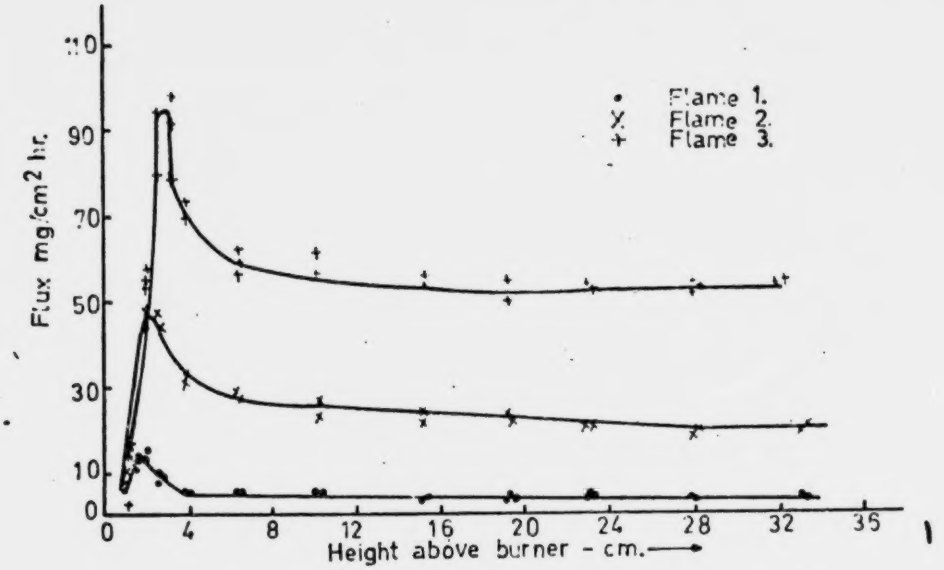


IV. Figure 1.6 Flux of total polymeric material vs. height above burner surface.

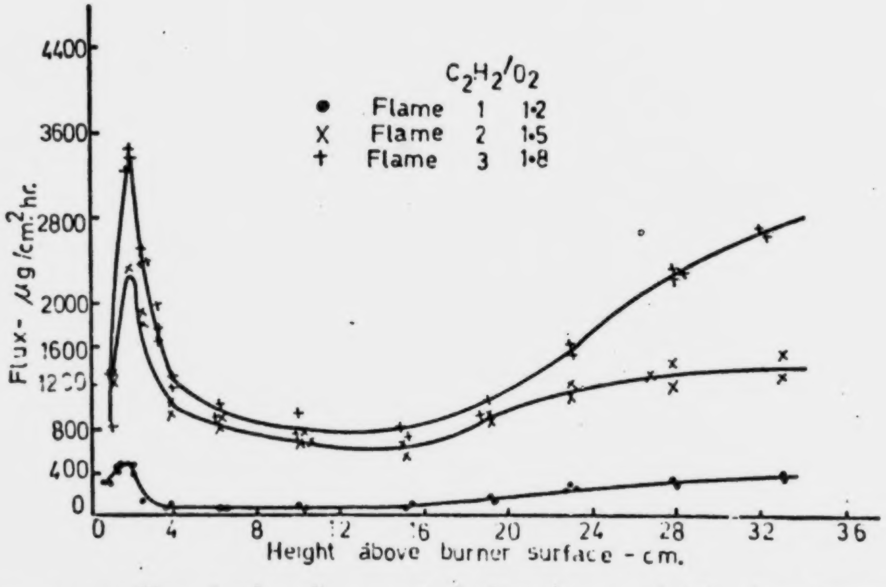


IV. Figure 1.7 Flux of soluble material vs. height above burner surface.

(Reproduced from Reference 2)

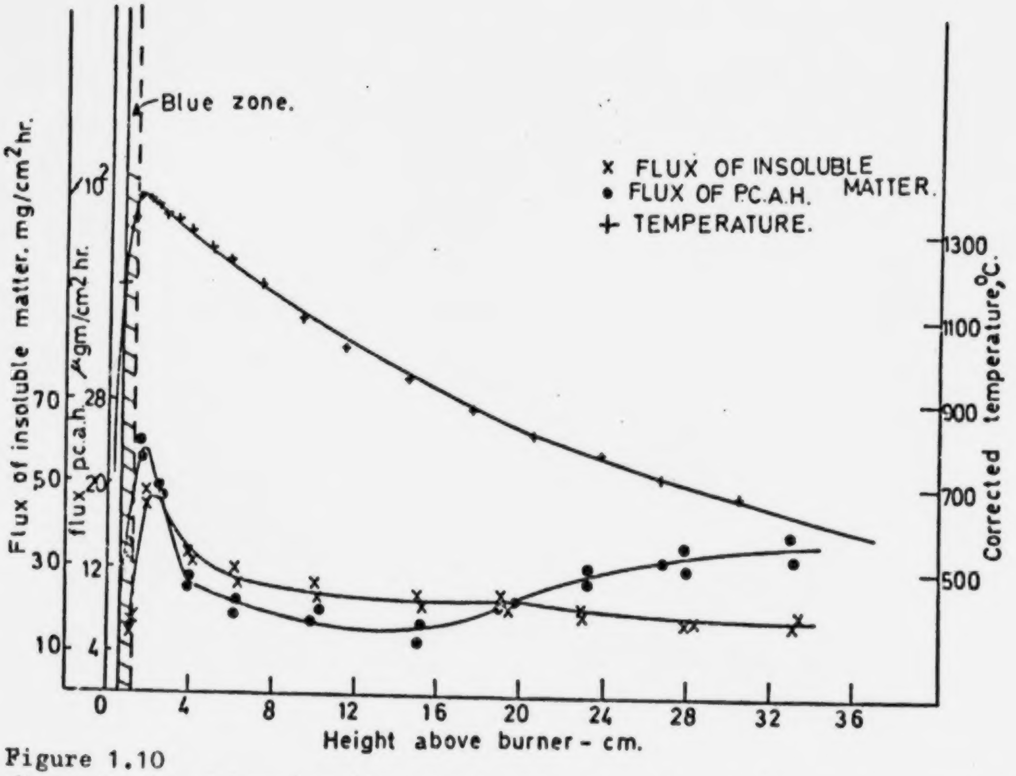


IV. Figure 1.8 Flux of insoluble material vs. height above burner surface.



IV. Figure 1.9 Flux of polycyclic aromatic hydrocarbons vs. height above burner surface.

(Reproduced from Reference 2)



IV. Figure 1.10

Composite plot of flux of insoluble material, flux of p.c.a.h. and of temperature respectively vs. height above burner surface. (for Flame 2).

(Reproduced from Reference 2)

IV. **TABLE 1.1** Range of polycyclic aromatic hydrocarbons identified by Tompkins and Long[7].

	p.c.a.h. identified	Mass no. by mass spectrometry
1	naphthalene derivatives (?)	-
2	acenaphthylene	152
3	fluorene	166
4	acenaphthene	154
5	acenaphthylene derivatives (?)	166 and 176
6	phenanthrene (ca. 80%) + anthracene (ca. 20%)	178
7	4,5-methylene phenanthrene	190
8	fluoranthene	202
9	fluoranthene isomers (?)	202
10	pyrene	202
11	benzofluorenes (?)	216
12	methyl pyrenes	216
13	benzo-(m-n-o)-fluoranthene	226
14	benz(a)anthracene (ca.80%) + chrysene (ca.20%)	228
15	a pyrene derivative (?)	[illegible]
16	a benzanthracene derivative (?)	250
17	unidentified	258
18	benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthone (?)	252
19	benzo(e)pyrene, benzo(a)pyrene, perylene	252
20	benzopyrene derivative (?)	264

(?) indicates that identification is not certain hydrocarbons as reported by Homann and Wagner[1]. However, Tompkins and Long[2] have shown that the concentrations of the poah never actually decline to zero. These results apparently contradict those reported by Homann and Wagner since the majority of poah identified by Tompkins and Long are devoid of side chains and are thus probably rather unreactive.

The chloroform insoluble material which is formed early in the flame has an H/C ratio approximately equal to 1.05 which compares with that obtained by Homann and Wagner[1] for the 'carbon' particles formed just beyond the blue reaction zone. On account of the fact that the chloroform insoluble material low in the flame has an H/C ratio similar to that of the fuel itself, Tompkins and Long[2] thought it unlikely that this material could be formed from polyacetylenes; Homann[45], however, pointed out that higher polyacetylenes can easily add on smaller hydrocarbon radicals to form a larger radical which in turn can add on further acetylene with loss of some hydrogen to account for the H/C ratio of unity.

Fenimore, Jones and Moore[33] have worked with quenched flat flames of various fuel and oxygen mixtures at various pressures to find that in an oxy-ethylene flame, the ratio of methane to acetylene in the burned gas is about 0.3, whilst in an oxy-acetylene flame no methane can be detected. In both flames they found that the ratio of benzene to acetylene in the burned gas is 0.006 ± 0.002. It is interesting to note that these workers did not find a burned gas (from the fuels they employed) which is free of acetylene, thus emphasising the possible importance of this compound in flame chemistry.

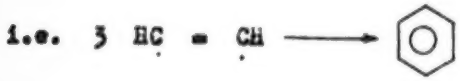
1.2 Hypotheses of Polycyclic Aromatic Hydrocarbon Formation

Various hypotheses have been proposed for the formation of poah from simple fuel molecules, a certain amount of emphasis having been laid on compounds considered to be precursors of the poah. The rôles of compounds such as acetylene, ethylene and 1.3-butadiene and their corresponding radicals are discussed in sections 1.2.1 to 1.2.4.

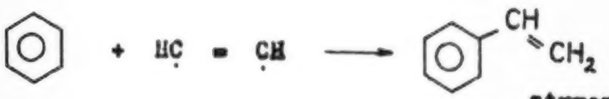
1.2.1 The Rôle of Acetylene

The possible importance of acetylene in the chemistry of rich premixed flat flames has been pointed out earlier (Section 1.1.4).

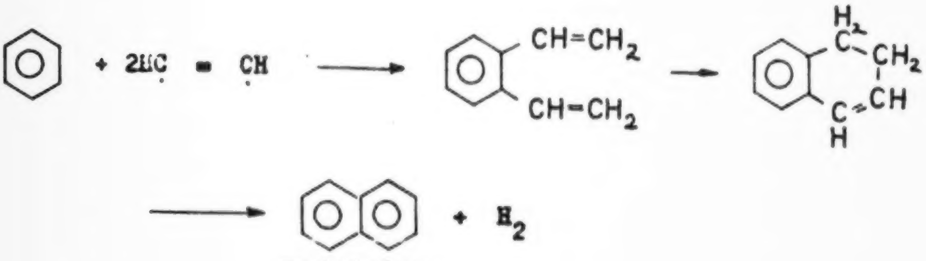
Groll[46] considered the divalent radicals of acetylene ($H\underset{\cdot}{C} = \underset{\cdot}{C}H$) and acetylenic compounds ($R\underset{\cdot}{C} = \underset{\cdot}{C}H$) to be important precursors of poah in the vapour phase pyrolysis of hydrocarbons. He considered that a species such as $H\underset{\cdot}{C} = \underset{\cdot}{C}H$ would more readily polymerise to benzene rather than form acetylene



Groll proposed the following schemes for the formation of styrene (a significant product in the pyrolysis of propylene) and naphthalene:



styrene

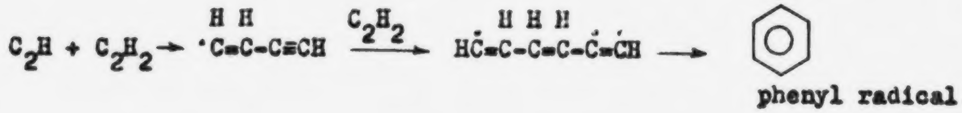


naphthalene

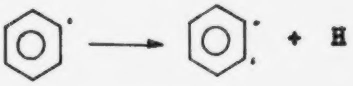
He also proposed that pcah such as anthracene and phenanthrene might be formed via similar mechanisms.

Stehling, Frazee and Anderson[47] have considered it unlikely that acetylene would polymerise directly to benzene which would then react further in the manner proposed by Groll[46], since benzene is not very reactive. Instead, Stehling et al[47] have suggested the following free radical processes for the formation of the phenyl radical and other aromatic species:

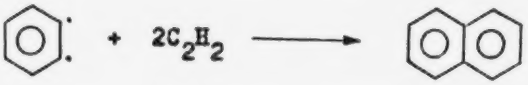
(i)



Sufficient energy might then be released for:



and

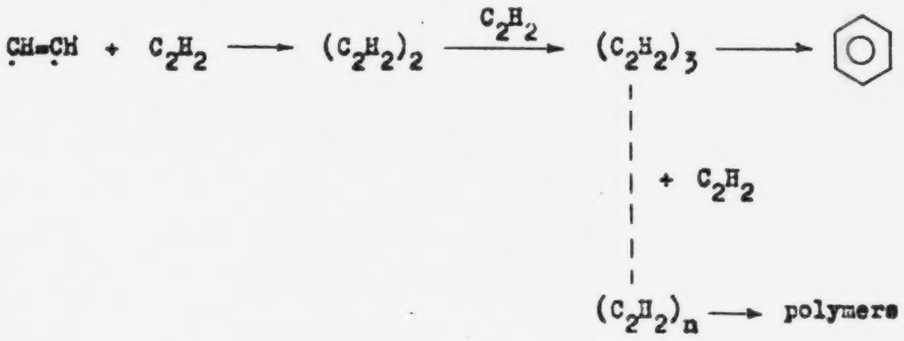


(ii)
$$\cdot C_2H + C_2H_2 \longrightarrow \cdot\overset{H}{C}=\overset{H}{C}-C\equiv CH \xrightarrow{C_2H_2} \cdot\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-C\equiv C$$

$$\longrightarrow \begin{cases} \cdot CH=CH-CH=CH-CH=CH-CH\equiv CH \\ CH\equiv C-CH=CH-\underset{\cdot}{C}=\underset{\cdot}{C}-C\equiv CH + H \end{cases}$$

Hydrogen stripping could then occur together with condensation to aromatic molecules.

Cullis, Minkoff and Nettleton[48] have proposed the following reaction mechanism to account for the formation of polymeric material in the pyrolysis of acetylene



In more recent work Cullis and Franklin[49] have proposed a similar mechanism for the polymerisation process which involves the electronically excited triplet state of acetylene (denoted $C_2H_2^*$) rather than the free-radical ĊH=ĊH

$$C_2H_2 \overset{\text{surface}}{\rightleftharpoons} C_2H_2^*$$

$$C_2H_2 + C_2H_2^* \rightleftharpoons C_4H_4^*$$

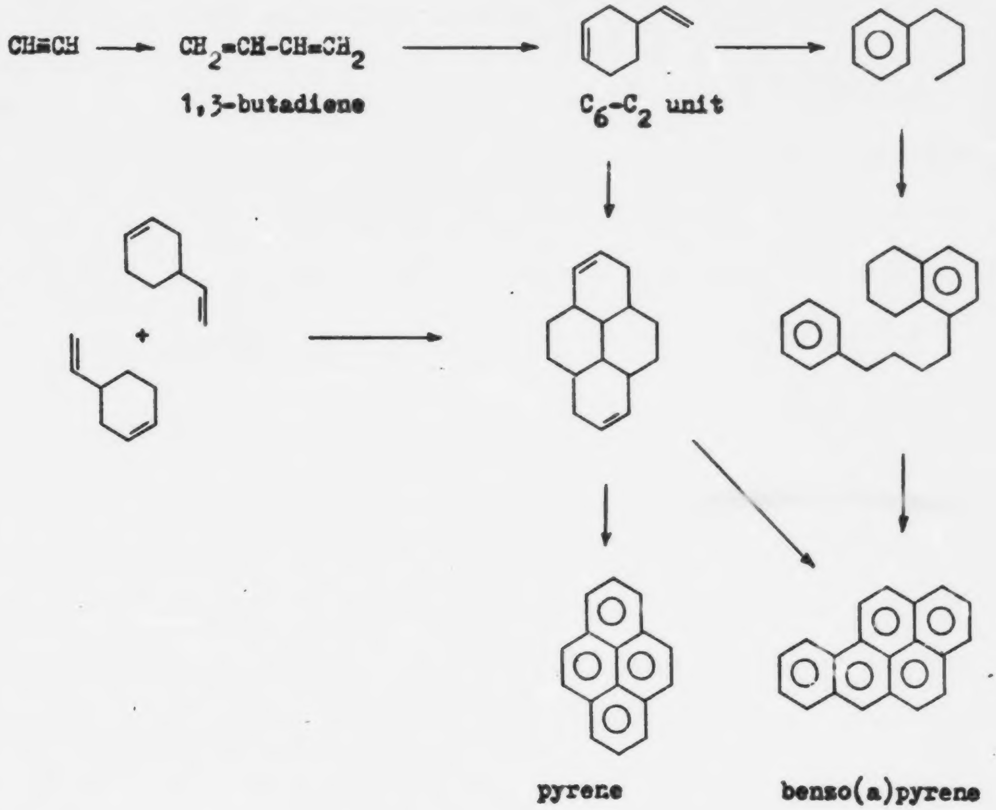
$$C_4H_4^* \overset{\text{surface}}{\rightleftharpoons} C_4H_4 \quad \text{(vinylacetylene)}$$

The existence of other species may be explained thus:

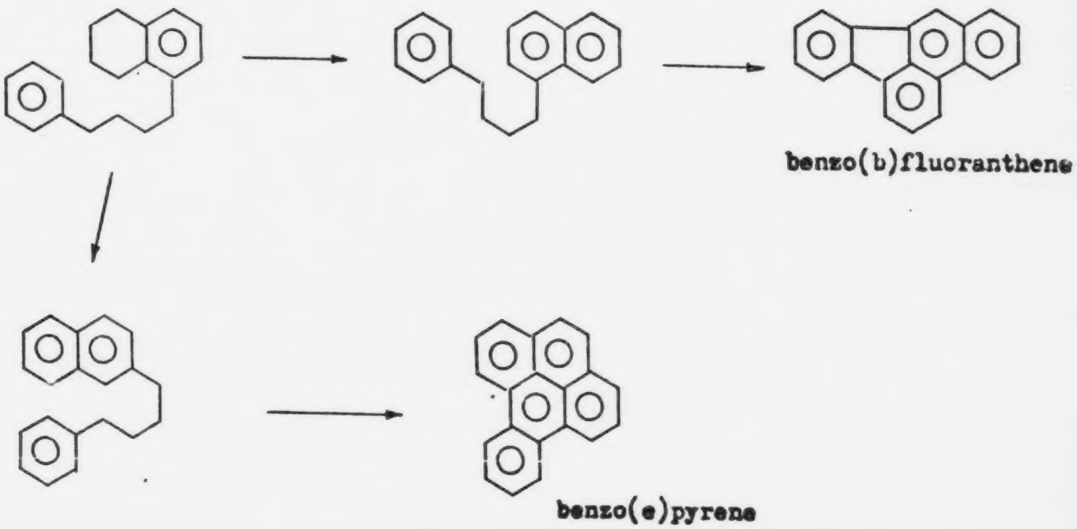
$$C_4H_4^* + C_2H_2 \rightleftharpoons C_6H_6^*$$

$$C_6H_6^* + C_2H_2 \rightleftharpoons C_8H_8^* \quad \text{etc.}$$

Badger[50] has proposed a step-wise mechanism for the formation of various pcah from acetylene during pyrolysis:


CH≡CH
CH2=CH-CH=CH2
1,3-butadiene
C6-C2 unit
+
pyrene
benzo(a)pyrene

Other pcah might be formed thus[51]:


benzo(b)fluoranthene
benzo(e)pyrene

Badger[50] has pointed out that such mechanisms may not be the only ones important in the formation of any one pcah and that other species might also be formed by decomposition of any of the above mentioned species to a variety of free-radicals which might react in different ways.

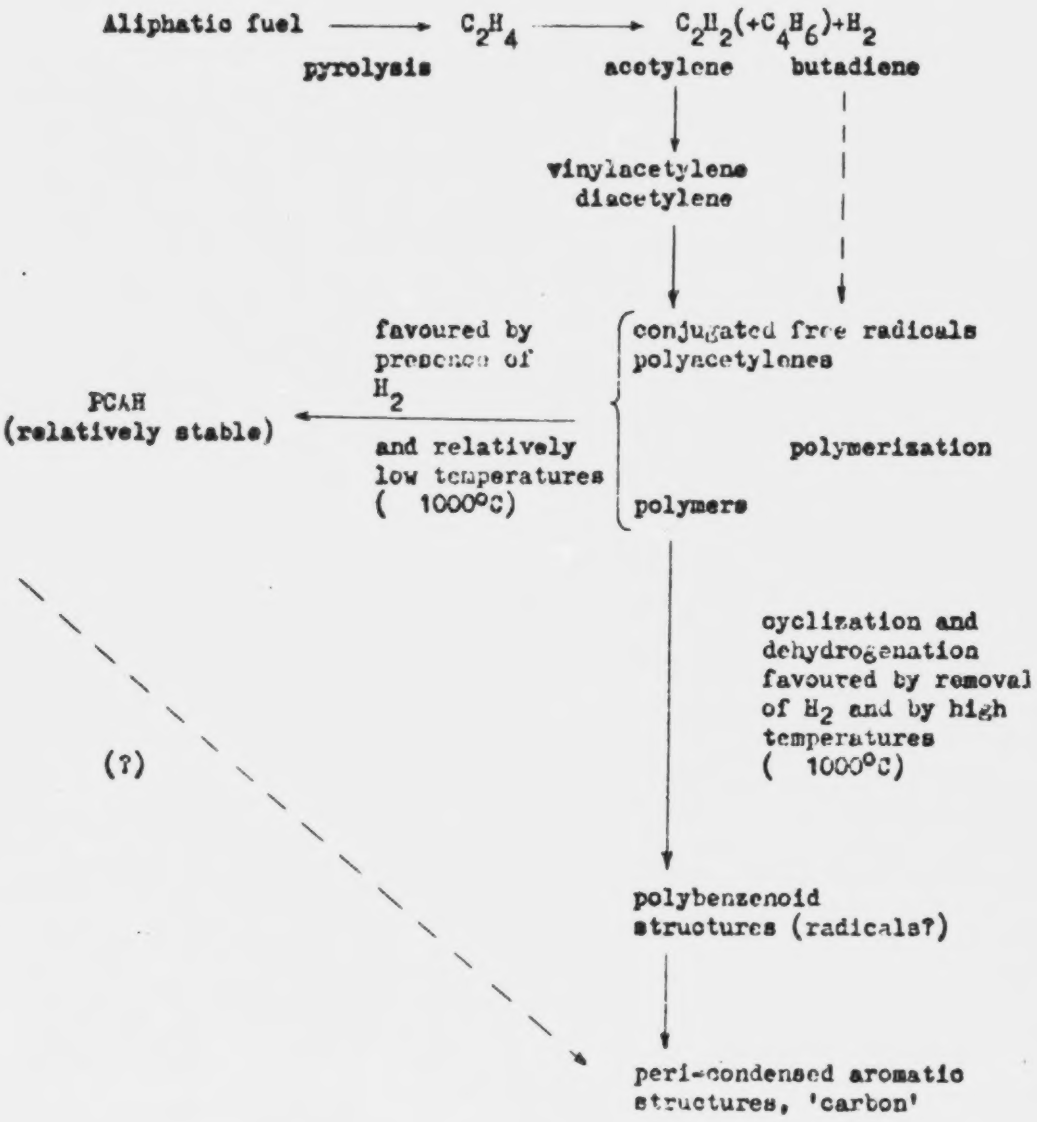
Although the importance of species such as acetylene and the acetylenyl radical in the flame chemistry have been pointed out by Fenimore et al[33] and Anderson[52], the results of Bonne Homann and Wagner[35] show also that the fuel is initially broken down at least partially into C_1 fragments to form C_3 species such as methylacetylene and propylene.

Chakraborty and Long[53] have presented the reaction scheme shown in Figure 1.11 to account for the formation of pcah and 'carbon' in their experiments on diffusion flames[53-55] and the work of others in this laboratory[2,56]. Although it is apparent that no specific mechanism can account for their results, Dearden and Long[56] were able to show, however, that acetylene is a significant reaction product in rich ethylene and propane diffusion flames.

Since 'carbon' does not arise preferentially from a two-carbon fragment in explosion flames of propane-2-^{13}C[57] and since the presence of the $\dot{C}H$ radical has been established in flames[58], Lindsey[18] has suggested that pcah might be formed either directly from the $\dot{C}H$ radical or indirectly via acetylene.

1.2.2 The Rôle of Ethylene

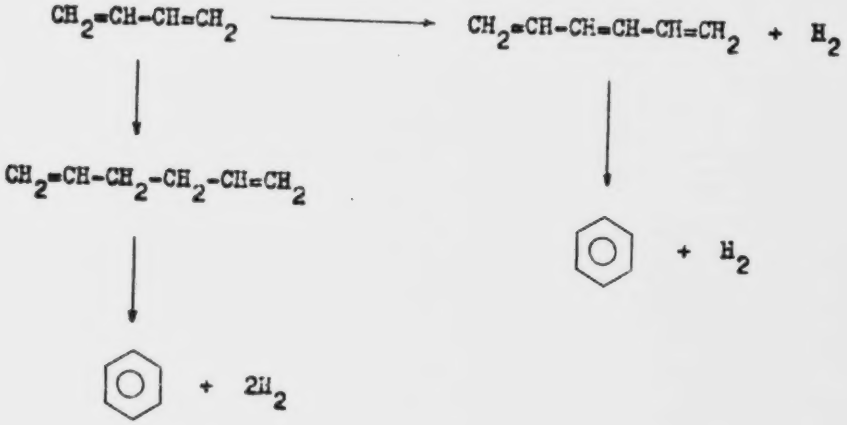
In their research on the pyrolysis of paraffins, Hague and Wheeler[59] found that the production of ethylene reaches a maximum at temperatures


Aliphatic fuel
C_2H_4
$C_2H_2(+C_4H_6)+H_2$
pyrolysis
acetylene
butadiene
vinylacetylene
diacetylene
favoured by
presence of
H_2
and relatively
low temperatures
(1000°C)
PCAH
(relatively stable)
conjugated free radicals
polyacetylenes
polymerisation
polymers
cyclization and
dehydrogenation
favoured by removal
of H_2 and by high
temperatures
(1000°C)
(?)
polybenzenoid
structures (radicals?)
peri-condensed aromatic
structures, 'carbon'

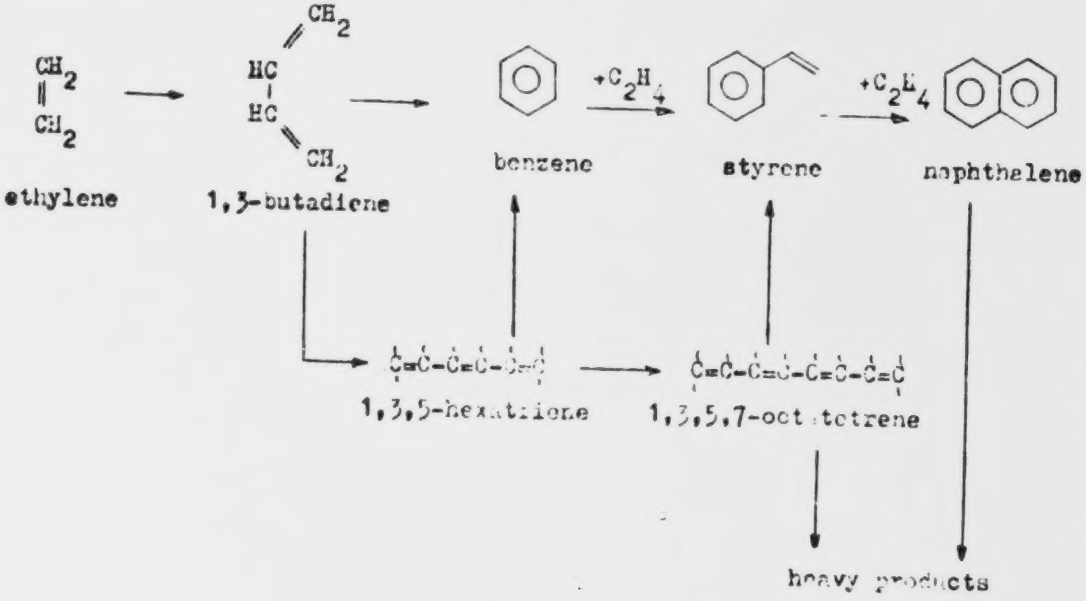
IV. Figure 1.11 Reaction Scheme Presented by Chakraborty and Long[53] to account for the Formation of PCAH and 'Carbon' in Diffusion Flames.

between 700°C and 750°C. They also found that the yields of ethylene are proportional to the percentage yields of pcah formed later in the reactions leading them to believe that the following chain-lengthening and cyclisation mechanism might account for their results:

$$2\ C_2H_4 \longrightarrow \underset{\text{1-butene}}{CH_3\text{-}CH_2\text{-}CH{=}CH_2} \longrightarrow \underset{\text{1.3-butadiene}}{CH_2{=}CH\text{-}CH{=}CH_2} + H_2$$


CH2=CH-CH=CH2
CH2=CH-CH=CH-CH=CH2 + H2
CH2=CH-CH2-CH2-CH=CH2
+ H2
+ 2H2

This mechanism is very similar to that proposed by Kinney and Crowley[60], which has been reproduced, in part, below.

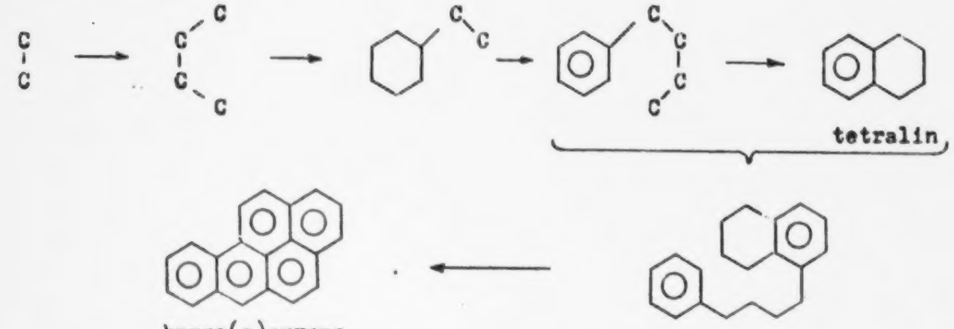

CH2
CH2
ethylene
CH2
HC
HC
CH2
1,3-butadiene
benzene
+C2H4
styrene
+C2H4
naphthalene
C=C-C=C-C=C
1,3,5-hexatriene
C=C-C=C-C=C-C=C
1,3,5,7-octatetrene
heavy products

The relatively high yield of toluene in the pyrolysis of C_2 and C_3 hydrocarbons is explained by the methylation of 1.3-butadiene; Kinney and Crowley[60] have suggested that methyl radicals might be formed directly from ethylene.

1.2.3 The Importance of a C_2 Species

The importance of a C_2 species in the formation of pcah from simpler molecules is significant since Oró and Han[61] report that about 97% of the total amount of aromatic hydrocarbons synthesised from methane at 1000°C is composed of hydrocarbons with even numbers of carbon atoms. This may be explained by the fact that at such high temperatures, acetylene and other C_2 species are thermodynamically more stable than methane and other C_1 species.

Badger and co-workers[62,63] have studied the formation of aromatic hydrocarbons at high temperatures, and as a working hypothesis suggested the following reaction scheme for the formation of a compound such as benzo(a)pyrene.



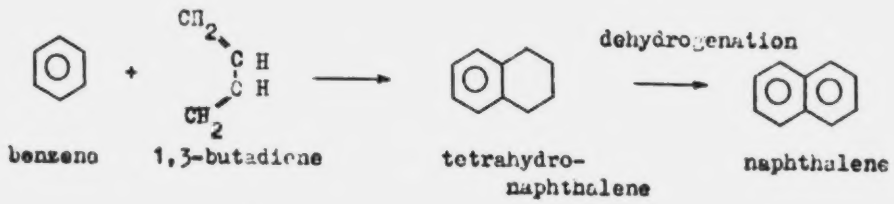
These workers have suggested that intermediates might be formed from fragments larger than a C_2 species and that complex hydrocarbons need not necessarily break down to C_2 species before re-synthesis to pcah.

However, the results of their pyrolysis experiments[44,51,64-85] with hydrocarbons which might be important intermediates in the formation of pcah show that similar products are obtained from the various tars produced. In several experiments both ethylene and methane were detected in the reactor gases, thus indicating that the fuel is initially broken down both to a C_1 and to a C_2 species.

All the reaction mechanisms reported in sections 1.2.1 and 1.2.2 with the exception of that proposed by Groll[46] indicate the initial formation of a C_4 species from a C_2 species. Of the C_4 species available only 1.3-butadiene has been seriously suggested in the past as being a possible precursor of pcah.

1.2.4 The Rôle of 1.3-butadiene

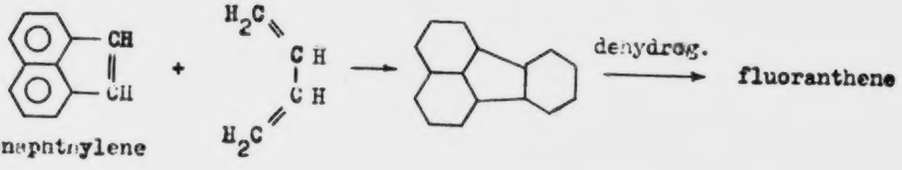
Meier zu Köcker[86] and Funugi and co-workers[87] have suggested that pcah are formed by Diels-Alder-type reactions between 1.3-butadiene and mono-olefines followed by dehydrogenation. This supports the hypotheses proposed earlier by Weizmann and co-workers[88] and Hague and Wheeler[59] who have included also the possibility of butadiene reacting with benzene-ring structures. For example, they have proposed that naphthalene might be formed in the following manner from benzene and 1.3-butadiene.



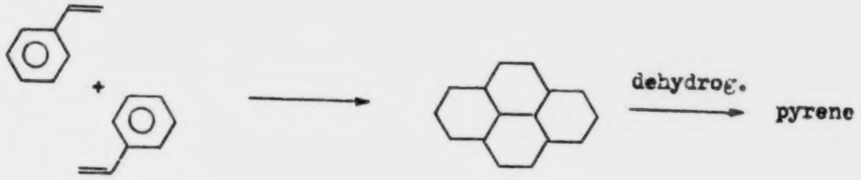
Anthracene and phenanthrene might also be formed in this manner from naphthalene.

Weizmann et al[88] also suggest that (a) fluoranthene might be formed from acenaphthylene, (b) pyrene might be formed from styrene and (c) chrysene might be formed from indene by the following mechanisms.

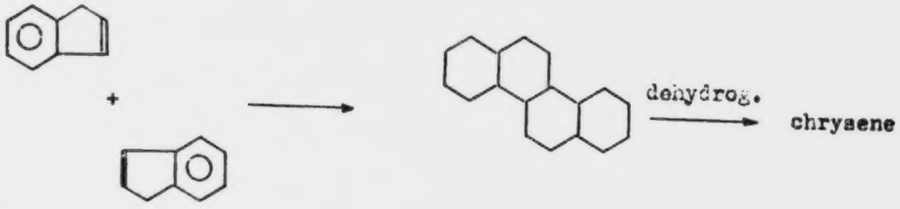
(a)


CH
CH
acenaphthylene
+
H2C
C H
C H
H2C
dehydrog.
fluoranthene

(b)


+
dehydrog.
pyrene

(c)


+
dehydrog.
chrysene

Mechanism (a) is supported by the results of Bergmann[89] and Kloetzel and Mertel[90] who have found that acenaphthylene reacts readily at temperatures between 140°C and 200°C with dienes to yield hydrogen substituted fluoranthene derivatives.

An objection to the diene synthesis reactions for the formation of pcah has been raised by Badger and Spotswood[72] who have found that there is no significant increase in the yields of benzo(a)pyrene and benzo(e)pyrene when 1.3-butadiene is pyrolysed in the presence of pyrene vapour at 700°C.

From the results of their work on the thermal decomposition of ethylene at temperatures between 977° and 1577°C Kozlov and Knorre[91] have concluded that butadiene which is first formed from ethylene is subsequently decomposed to acetylene:

$$C_2H_4 + C_2H_4 \longrightarrow \underset{\text{1-butene}}{C_4H_8} \longrightarrow \underset{\text{butadiene}}{C_4H_6} + H_2$$

$$C_4H_6 \longrightarrow C_2H_2 + C_2H_4$$

1.5 Summary of Chapter 1

The results of previous research both on polycyclic aromatic hydrocarbon and 'carbon' formation in rich premixed flat flames suggest that the fuel is initially broken down, in part, to both C_1 and C_2 units. Higher molecular weight species might then be formed by chain lengthening processes similar to those which have been proposed by Hague and Wheeler[59], Kinney and Crowley[60] and Stehling et al[47]. These long-chain molecules, by a process of dehydrogenation and cyclisation might account for the formation of pcah and other aromatic molecules in rich premixed flat flames. The chain lengthening processes are evident in the results of Homann and co-workers[35] and Kistiakowsky and co-workers[128]; it is well-known, also, that polyacetylenes are unstable compounds and readily polymerise[159-161]. Homann and co-workers[35] think it likely that the polyacetylenes which are found in rich premixed hydrocarbon flames might be precursors of 'carbon' although it is possible that such molecules are by-products of other reactions.

Both acetylene and ethylene (and their corresponding radicals) have been proposed as intermediates in the formation of pcah although Homann's results suggest that acetylene is the more important species. Pyrolysis of residual acetylene in rich premixed flat flames might account for the secondary region of formation of pcah[2], especially since temperatures within this region are favourable for pcah formation generally[44].

1,3-Butadiene is present in relatively small concentrations in the reaction zone of rich premixed oxy-acetylene and oxy-ethylene flames[39], but under the conditions encountered in the blue zone of such flames it is likely that butadiene would decompose to acetylene rather than polymerise (section 1.4.7). The absence of other olefinic compounds, notably the cyclic compounds, suggests that the pyrolysis of ethylene does not occur within the flame.

The results from the pyrolysis of acetylene show that at high temperatures and at short contact times diacetylene formation is favoured and the presence of relatively large amounts of this compound in the blue reaction zone of rich premixed flames suggests that the following overall reaction might occur.

$$2\,C_2H_2 \longrightarrow C_4H_2 + H_2$$

Vinylacetylene, which is formed prior to diacetylene in the reaction zone of such flames is formed generally at lower temperatures under pyrolysis conditions.

The fact that biphenyl and other poly-phenyls have not been found in measurable quantities both in rich premixed[2] and in rich diffusion[17,18, 53-55,162] flames suggests that benzene pyrolysis does not occur and that this compound is a relatively stable by-product. The relative unreactivity of benzene and pcah such as naphthalene, anthracene, pyrene, etc., suggests that the pcah which are present in flame soots are likely to be side-products rather than important intermediates in the formation of 'carbon'. However, once formed, polycyclic aromatic hydrocarbons may well be pyrolysed to some extent in the burned gases in the flame to produce species of higher molecular weight and possibly carbonaceous material also.

The works of Arthur and co-workers[17] and Lindsey[18] show that similar pcah, although in differing quantitative distributions, are formed in diffusion flames of a wide variety of fuels. This suggests that these compounds are stable by-products of the flame (cf. Group 2 hydrocarbons in

Homann's work) and that the actual mechanism of formation may be different for each fuel.

There is some uncertainty as to the nature of the reactive poah (Group 3) which Homann and co-workers have claimed exist in the blue reaction zone of premixed flat flames although it is accepted that the more stable poah which may be extracted from flame soots are devoid, generally, of side-chains. Recent work carried out by Kern and Spengler[162] has shown that species such as phenylacetylene, styrene and toluene exist in the gases of rich hexane diffusion flames.

IV - 2

Experimental

The burner employed is of the type used originally by Botha and Spalding[25] and later by Homann and co-workers[27,28] to stabilize flat flames of various rich fuel/oxygen mixtures at reduced pressure and also by Tompkins[36] for rich C_2H_2/O_2 flames.

Samples are withdrawn from the flame via fused silica microprobes in two distinct ways as shown in Figure 2.1.

The batch collection system enables the major products of the flame (i.e. hydrogen, water, carbon monoxide, carbon dioxide, etc.) to be sampled quickly and efficiently. The continuous flow collection system allows samples to be withdrawn from the flame over relatively long periods, thus enabling sufficient quantities of species such as polycyclic aromatic hydrocarbons to be collected for subsequent analysis.

IV - 3

Analytical Methods

Full details of the mass spectrometric and gas chromatographic analyses of the samples are given in the Ph.D. thesis of B. D. Crittenden.

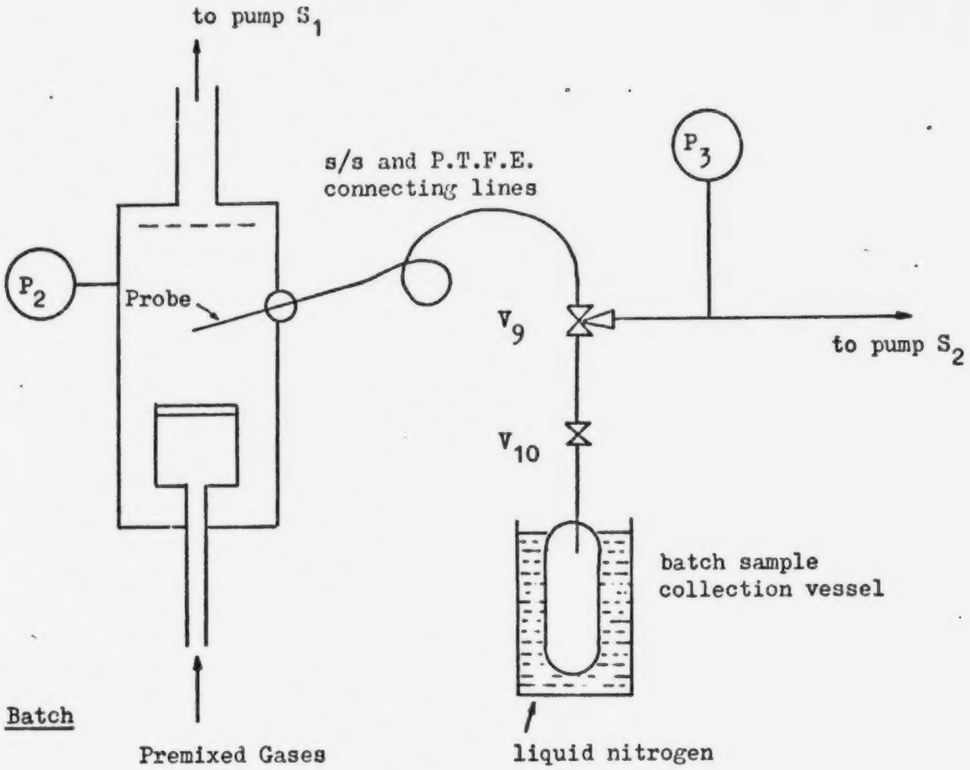
IV - 4

Results and Discussion

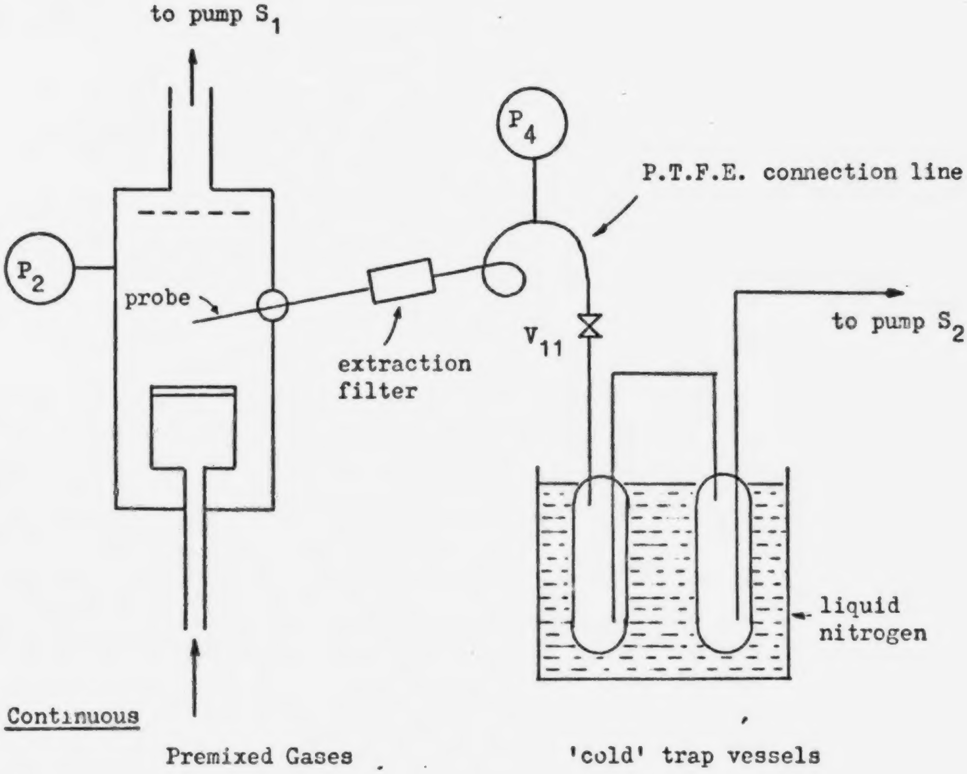
IV - 4 - 1 Introduction.

IV - 4 - 2 Temperature measurements.

IV - 4 - 3 Batch and Continuous Sampling - Results and Discussion


to pump S_1
s/s and P.T.F.E. connecting lines
P_3
P_2
Probe
V_9
to pump S_2
V_{10}
batch sample collection vessel
Premixed Gases
liquid nitrogen

(a) Batch


to pump S_1
P_4
P.T.F.E. connection line
P_2
probe
extraction filter
V_{11}
to pump S_2
liquid nitrogen
Premixed Gases
'cold' trap vessels

(b) Continuous

IV. Figure 2.1 Sample Collection Systems

IV - 4

Results and Discussion

4 - 1 Table 4. 1 shows the types of flame examined and the types of sample withdrawn from them. It was not possible to obtain quantitatively reproducible results from the batch samples unless argon was introduced into the flame as an "internal standard".

In the flames there were geometrical effects caused by the column of hot gases contracting as they became cooler. Since the change in density may be assumed to have the same effect on the concentrations of all species, including argon, in the flames employed, the concentration (in mole fractions) of species obtained from the batch sampling results are the actual mole fractions in the flame gases. However, in the continuous sampling method, species are withdrawn from the flame with no reference to the flame "internal standard". Consequently, high in the flame gases, concentrations of species are apparently too large and corrections must be applied to take the change in density into account.

In this study the height above the burner at which the flame in question has its maximum cross-sectional area is taken to be the reference height, h max. If the diameter of the flame at height h max is d max and the measured concentration at a sampling height h, (where the flame diameter is dh) is X, then the concentration corrected for the geometrical effects : X' is given by

$$X' = X. \left(\frac{d_h}{d_{max}}\right)^3$$

Table 4.1

Flames Employed in this Study

Flame	1	2	3	4	5	6
C_2H_2 flow l/min NTP	3.58	-	3.58	3.32	-	3.32
C_2H_4 flow l/min NTP	-	3.58	-	-	3.32	-
O_2 flow l/min NTP	2.76	2.76	2.76	3.02	3.02	3.02
Ar flow l/min NTP	0.5	0.5	-	0.5	0.5	-
Total flow l/min NTP	6.84	6.84	6.34	6.84	6.84	6.34
Mixture strength	0.308	0.254	0.308	0.364	0.303	0.364
Fuel/oxygen ratio	1.3	1.3	1.3	1.1	1.1	1.1
Pressure mm Hg	40	40	40	40	40	40

Types of Sample Collected

Flame	1	2	3	4	5	6
Batch	✓	✓		✓	✓	
Continuous 'cold' trap	✓	✓	✓			✓
Continuous filter extract	✓	✓	✓			

The term $\left(\frac{d_h}{d_{max}}\right)$ is cubed since the geometrical effects are caused by a change in density of the hot column of gases. Figure 4.1.3 shows a plot of $\left(\frac{d_h}{d_{max}}\right)^3$ versus the height above the burner surface for Flames 1, 2, 3, 4, 5, and 6 together with the values of d_{max}.

In all the flames studied there is no indication of a 'dark space' as has been observed by several workers. The oxidation or blue zone of oxy-acetylene flames is a blue-green colour although it is referred to in the text as being blue. The oxidation zone of an oxy-ethylene flameis, in fact, blue.

The flames listed in Table 4.1 have been chosen so that direct comparisons may be made between similar oxy-acetylene and oxy-ethylene flames which have been run both at different fuel/oxygen ratios and also at different mixture strengths.

The mixture strength, λ, is defined as:

$$\lambda = \frac{\text{stoichiometric fuel/oxygen ratio}}{\text{actual fuel/oxygen ratio}}$$

IV - 4 - 2

Temperature Measurements

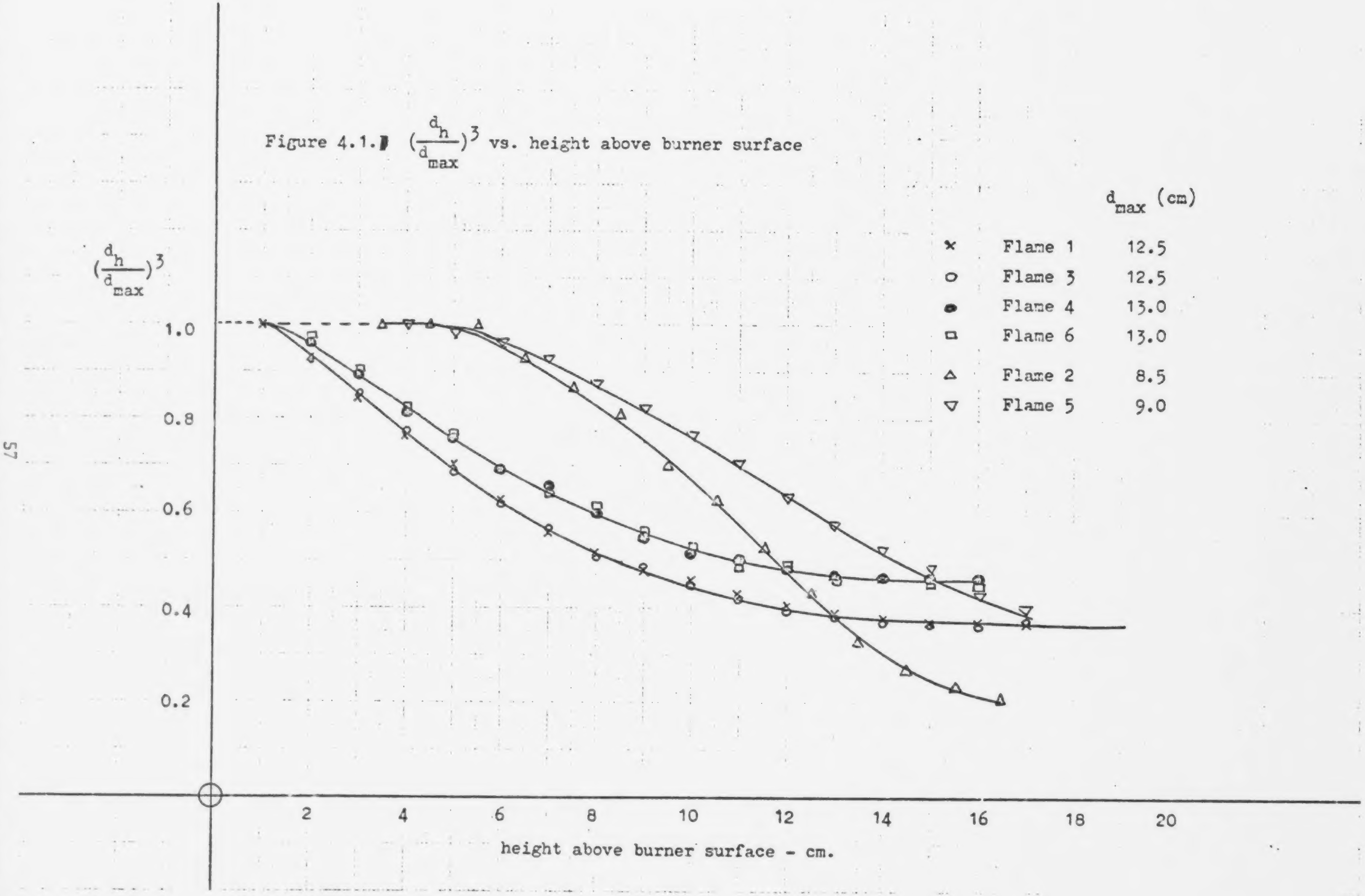
Temperatures were measured by fine wire, platinum: platinum 13% rhodium thermocouples and the results were corrected to zero hot junction diameter. [(Waggener(235)] Measurements were made at discrete positions in the oxy-acetylene and oxy-ethylene flat flames and the results are shown in Figures 4.2.1 and 4.2.2.

It is apparent that :-

i) the maximum temperature occurs just beyond the blue oxidation zone

ii) the addition of argon reduces the temperature

Figure 4.1. $(\frac{d_h}{d_{max}})^3$ vs. height above burner surface



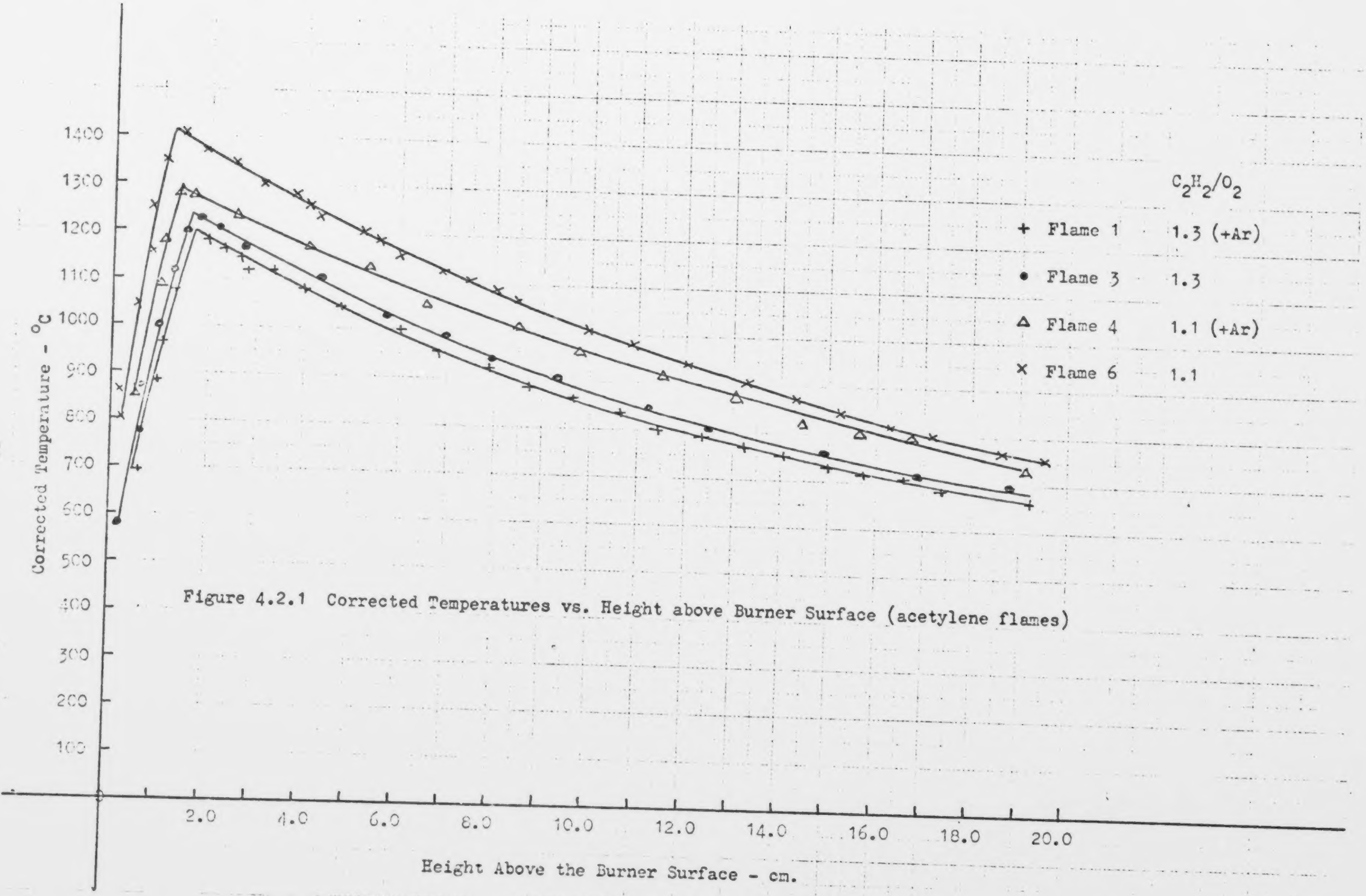


Figure 4.2.1 Corrected Temperatures vs. Height above Burner Surface (acetylene flames)

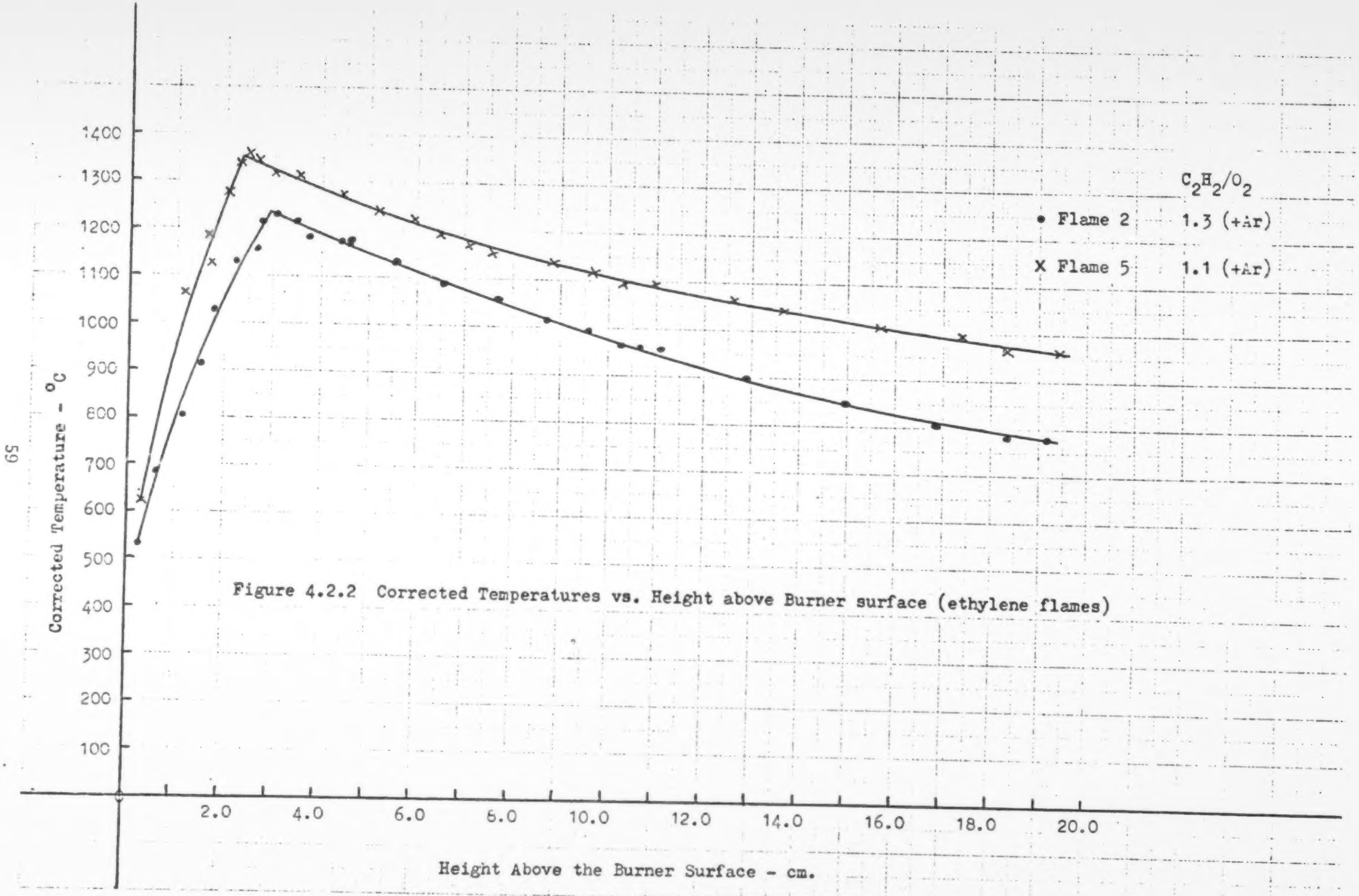


Figure 4.2.2 Corrected Temperatures vs. Height above Burner surface (ethylene flames)

iii) increasing the fuel/oxygen ratio decreases the temperature.

IV - 4-3 Batch and Continuous Sampling Results & Discussion

Since quantitative determinations using the MS9 mass spectrometer were achieved only by use of an argon 'standard' in the flame. The mole fractions of the species listed in Table 4.2 have been determined for Flames 1, 2, 4, and 5. Table 4.2 lists the nominal mass number, measured mass, and assignment for all species whose concentrations in the flame allow a peak intensity greater than that of the background signal to be recorded.

Figures 4.3.3 et seq show the mole fractions of various species in the flame as a function of sampling height above the burner.

Continuous Sampling Results

Identification of peaks in the gas chromatograms of the 'cold trap' products is listed in Table 4.3. The symbol (?) has been used to indicate that a peak has not been *positively* identified.

Preliminary identification of compounds present in the 'cold trap' samples was by mass spectrometry at both 70 eV and ∼10 e V. On the mass spectra which have been recorded at an ionising electron voltage of ∼10 (used so that there is negligible fragmentation 220) ions at the following mass numbers have significant intensities.

m/e = 78, 92, 102, 104, 106, 116, 118, 128, 130, 136, 142, 146, 152, 154, and 166.

Table 4.2

Mass Measurement and Assignment of Species Present in the Batch Samples

Nominal Mass		Measured Mass (eV)	Actual Mass (reference 242)	Assignment	
2	(NB 1)	not measured			Hydrogen
16	(NB 1)	" "			Methane
18	(NB 1)	" "			Water
26	(NB 1)	" "			Acetylene
28 I	(NB1,2)	" "			Carbon Monoxide
28 II	(NB1,2,5)	" "			Nitrogen
28 III	(NB1,2)	" "			Ethylene
32	(NB 1)	" "			Oxygen
40 I	(NB1,3)	" "			Argon
40 II	(NB 3)	40.031 (70)	40.031	$C_3H_4^+$	Methylacetylene/ propadiene
42		42.045 (70)	42.047	$C_3H_6^+$	Propylene
44	(NB 1)	not measured			Carbon Dioxide
50		50.015 (70)	50.016	$C_4H_2^+$	Diacetylene
52		52.032 (70)	52.031	$C_4H_4^+$	Vinylacetylene
74		74.013 (70)	74.014	$C_6H_2^+$	Triacetylene
78	(NB 4)	78.046 (70)	78.047	$C_6H_6^+$	Benzene

NB 1 Peaks at these m/e values have not been 'mass measured' since there is no ambiguity in their identification.

NB 2 The three peaks at m/e = 28 are usually separated on the photographic trace.

NB 3 The two peaks at m/e = 40 are usually separated on the photographic trace.

NB 4 The peak at m/e = 78 has been assigned to benzene rather than aliphatic molecules since benzene has been found to be present in the continuous collection samples.

NB 5 Nitrogen is present in the mass spectrometer as part of the 'residual air' (see Section 3.1.3.2.2.2).

Table 4.3

Identification of G.L.C. Peaks in the 'Cold' Trap Chromatograms

G.L.C. Peak	Compound Identified
1	unidentified solvent impurity
2	benzene
3	tetra-acetylene (?)
4	toluene
5	phenylacetylene
6	styrene
7	methyl styrenes (?)
8	trimethylbenzenes (?)
9	indene
10	unidentified
11	dihydronaphthalenes (?)
12	naphthalene
13	1-methyl naphthalene
14	biphenyl
15	acenaphthylene
16	fluorene

(?) denotes that this compound has not been positively identified.

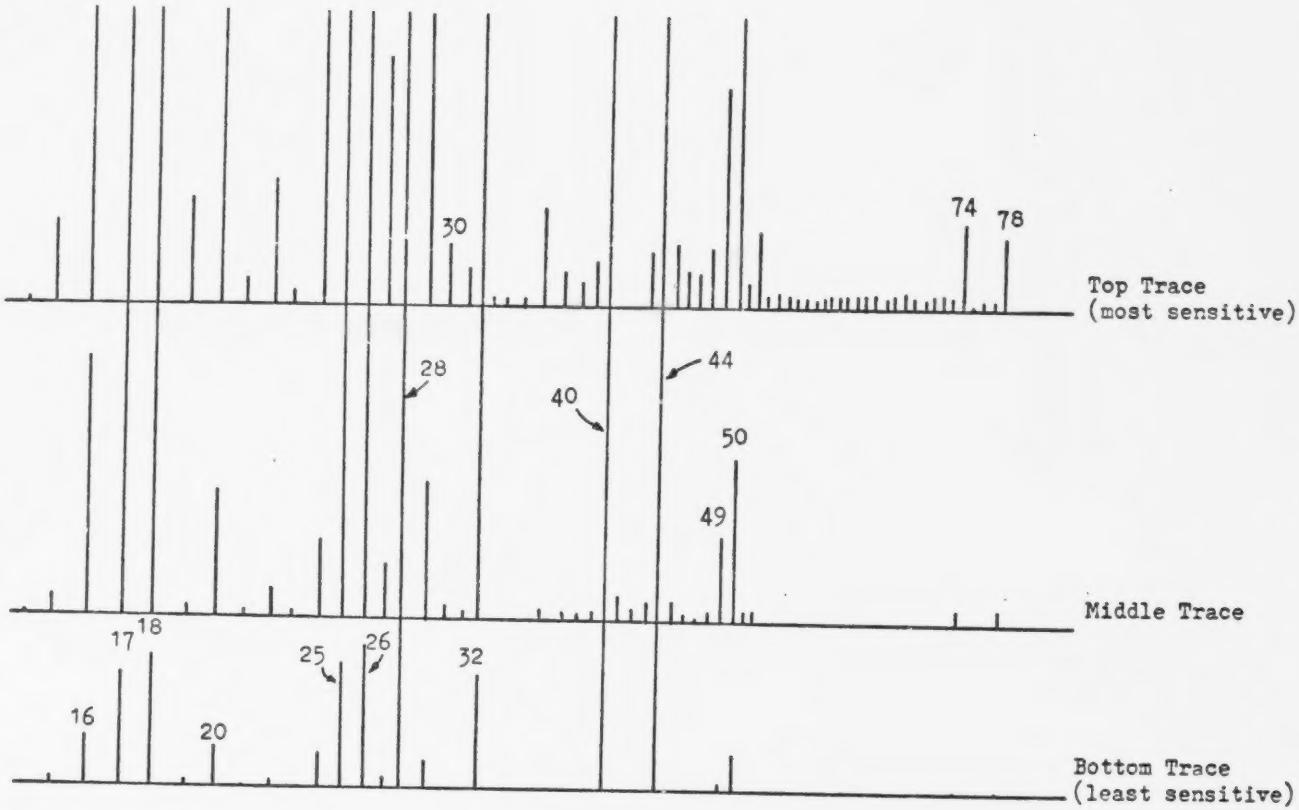


Figure 4.3.I. Part of a mass spectrum which results from the introduction of a typical batch sample into the source of the GEC-AEI MS9 mass spectrometer

N.B. The spectrum has been recorded (at 70eV) at an increased speed (for reproduction purposes) so that the resolution of the three peaks at m/e = 28 is not observable.

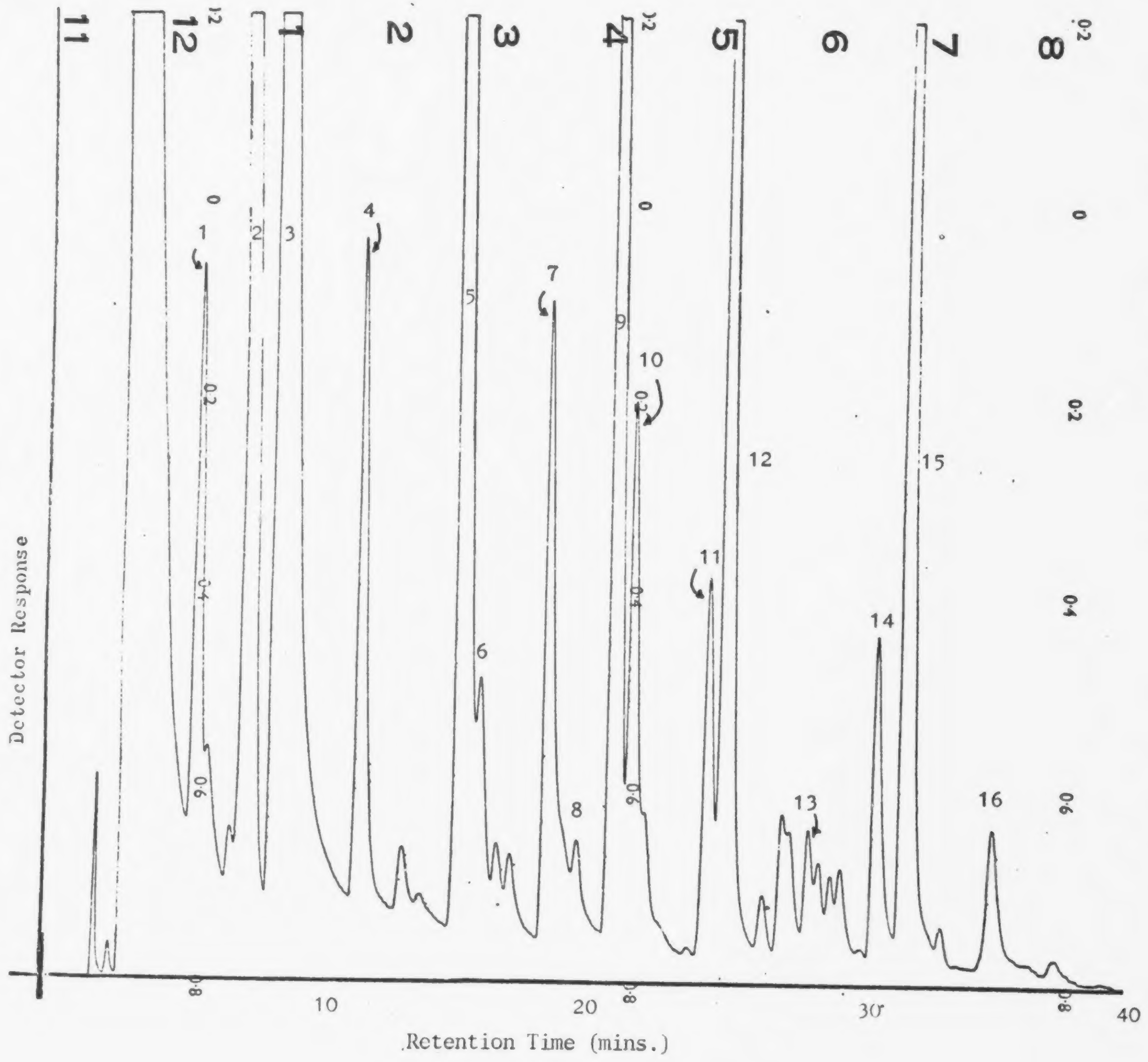


Figure 4.3.II

Chromatogram of 'Cold' Trap Sample Collected from Flame 1 at a sampling height of 18.7 cm. (25 µl injection)

The Identification of numbered peaks is given in Chapter 4.

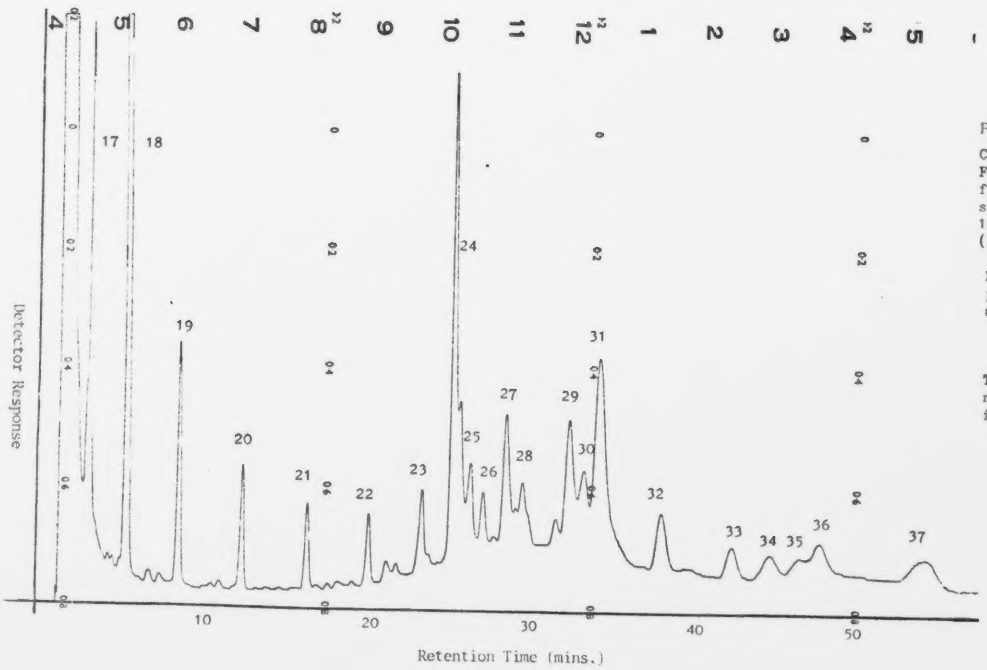


Figure 43.III.

Chromatogram of Extraction Filter Sample Collected from Flame 2 at a sampling height of 16.5 cm.
(25 µl. injection)

N.B. No 3-methyl phenanthrene has been added to the sample

The Identification of numbered peaks is given in Chapter 4.

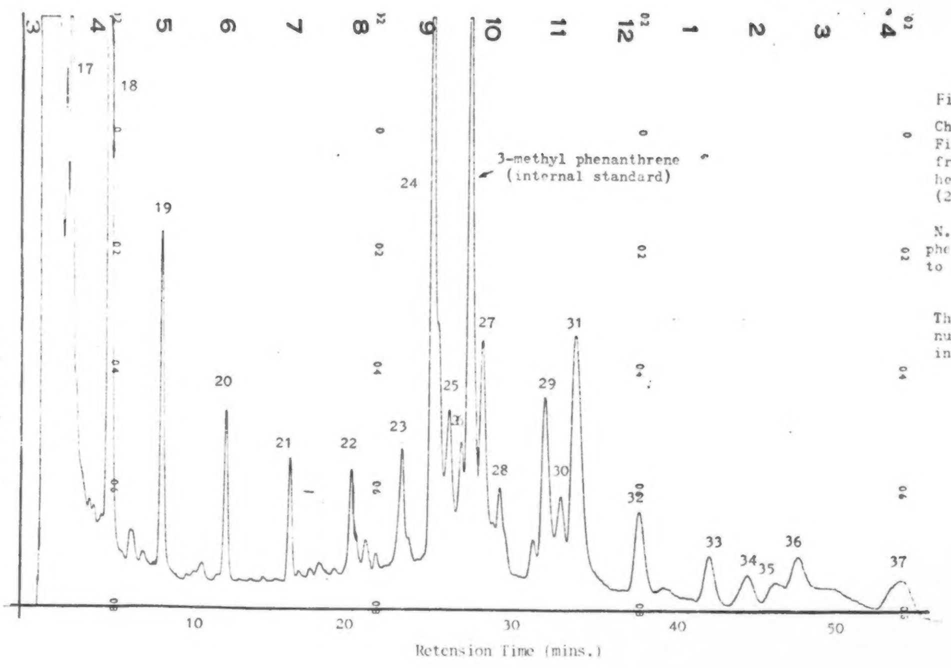


Figure 43.IV

Chromatogram of Extraction Filter Sample Collected from Flame 2 at a sampling height of 16.5 cm. (25 ul. injection)

N.B. 3-methyl phenanthrene has been added to the sample (cf.Figure [illegible]

The Identification of numbered peaks is given in Chapter 4.

Collection of Gas Chromatographic Fractions

For a positive identification of peaks in the gas chromatograms, fractions have been collected as they eluted from the chromatographic column for subsequent identification either by mass spectrometry or by ultra-violet absorption spectroscopy.

Concentration Profiles of 'Cold Trap' Products

Concentration profiles of several species are shown in Figures 4.4.1.3.4 et seq. The broken lines represent the concentrations of each species which would result if there were no geometrical effects due to the contraction of gases in the flame.

(Cf. Section IV - 4-1).

Identification of Gas Chromatographic Peaks in the Extraction Filter Samples

Preliminary identification of the species in the extraction filter samples has been carried out by introducing such samples in solution form into the source of the MS9 mass spectrometer via the direct insertion probe. On the mass spectra which have been recorded at 10 ev ions , at the following m/e values have significant intensities:

m/e = 116, 128, 130, 136, 142, 146, 152, 154, 166, 168, 176, 178, 190, 202, 216 and 226.

Each of the above ions has been 'mass measured' by comparision of its mass with that of an ion from the standard (heptacosafluoro - tri - n - butylamine) which has been introduced via the cold inlet system. The results are presented in Table 4.6.

Identification of gas chromatographic fractions from the extraction filter samples is summarized in Table 4.5.

Table 4.4

'Mass Measurement' of Mass Spectrum Peaks resulting from the 'Cold' Trap Samples

Nominal Mass	Measured Mass	Ionising (eV)	Actual Mass (ref. 242)	Assignment
78	78.046	(70)	78.047	$C_6H_6^+$
92	92.060	(70)	92.063	$C_7H_8^+$
102	102.044	(70)	102.047	$C_8H_6^+$
104	104.058	(70)	104.062	$C_8H_8^+$
106	106.074	(70)	106.078	$C_8H_{10}^+$
116	116.063	(70)	116.063	$C_9H_8^+$
118	118.074	(70)	118.078	$C_9H_{10}^+$
120	120.089	(70)	120.093	$C_9H_{12}^+$
128	128.060	(70)	128.062	$C_{10}H_8^+$
130	130.078	(70)	130.078	$C_{10}H_{10}^+$
136	136.126	(70)	136.125	$C_{10}H_{16}^+$
142	142.082	(70)	142.078	$C_{11}H_{10}^+$
146	146.108	(70)	146.110	$C_{11}H_{14}^+$
152	152.063	(70)	152.063	$C_{12}H_8^+$
154	154.079	(70)	154.078	$C_{12}H_{10}^+$
166	166.075	(70)	166.078	$C_{13}H_{10}^+$

Table 4.5

Identification of G.L.C. Peaks in the Extraction Filter Chromatograms

G.L.C. Peak	Compound Identified
17	unidentified solvent impurity
18	indene
19	naphthalene
20	1-methyl naphthalene
21	acenaphthylene
22	fluorene
23	1.8,4.5-bi-(etheno-)naphthalene (?)
24	anthracene + phenanthrene
25	unidentified
26	unidentified
27	4.5-methylene phenanthrene
28	unidentified
29	fluoranthene
30	a fluoranthene isomer
31	pyrene
32	benzofluorenes
33	methyl pyrenes
34	benzo(mno)fluoranthene
35	chrysene + benz(a)anthracene
36	a pyrene derivative (?)
37	unidentified

(?) denotes that this compound has not been positively identified

Table 4.6

'Mass Measurement' of Mass Spectrum Peaks Resulting from the Extraction Filter Samples

Nominal Mass	Measured Mass	ionising (eV)	Actual Mass (ref. 242)	Assignment
116	116.063	(70)	116.063	$C_9H_8^+$
128	128.060	(70)	128.062	$C_{10}H_8^+$
130	130.078	(70)	130.078	$C_{10}H_{10}^+$
136	136.126	(70)	136.125	$C_{10}H_{16}^+$
142	142.082	(70)	142.078	$C_{11}H_{10}^+$
146	146.108	(70)	146.110	$C_{11}H_{14}^+$
152	152.063	(70)	152.063	$C_{12}H_8^+$
154	154.079	(70)	154.078	$C_{12}H_{10}^+$
166	166.075	(70)	166.078	$C_{13}H_{10}^+$
168	168.055	(70)	168.057	$C_{12}H_8O^+$
176	176.059	(70)	176.063	$C_{14}H_8^+$
178	178.077	(13)	178.078	$C_{14}H_{10}^+$
190	190.078	(13)	190.078	$C_{15}H_{10}^+$
202	202.079	(13)	202.078	$C_{16}H_{10}^+$
216	216.096	(13)	216.093	$C_{17}H_{12}^+$
226	226.074	(13)	226.078	$C_{18}H_{10}^+$

Figure 4.3.3 (a)-(b) Acetylene Concentration Profiles

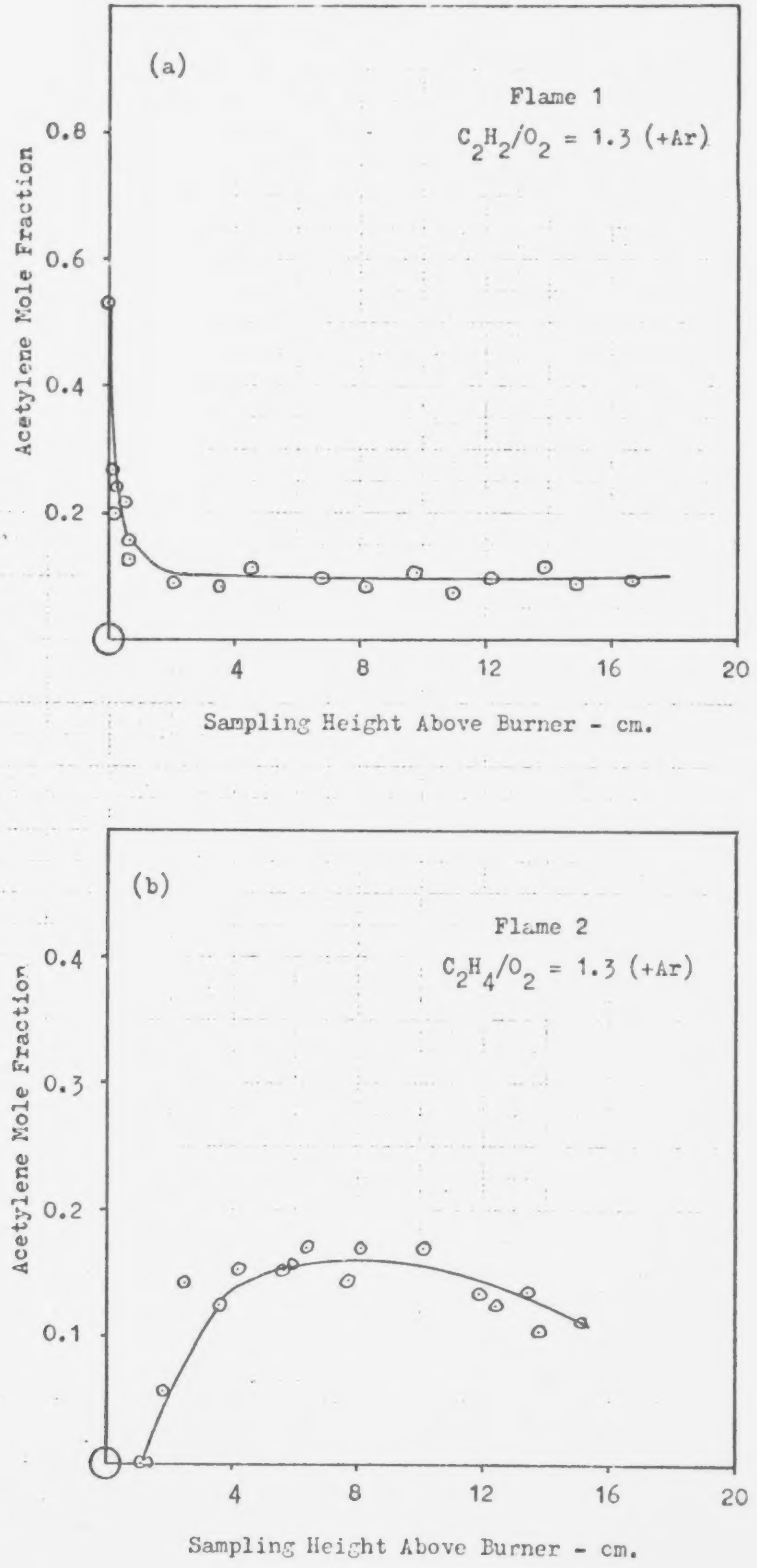
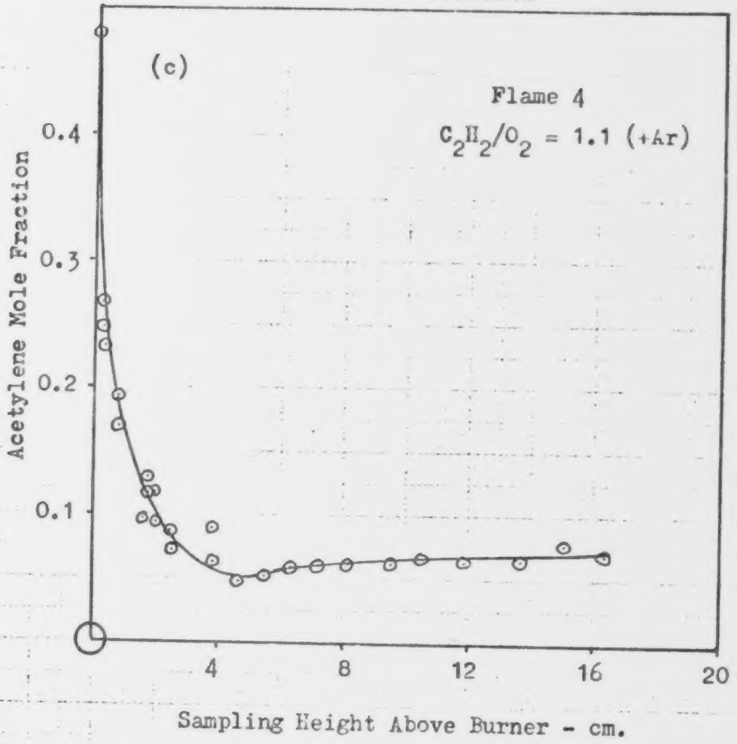


Figure 4.3.3 (c)-(d) Acetylene Concentration Profiles



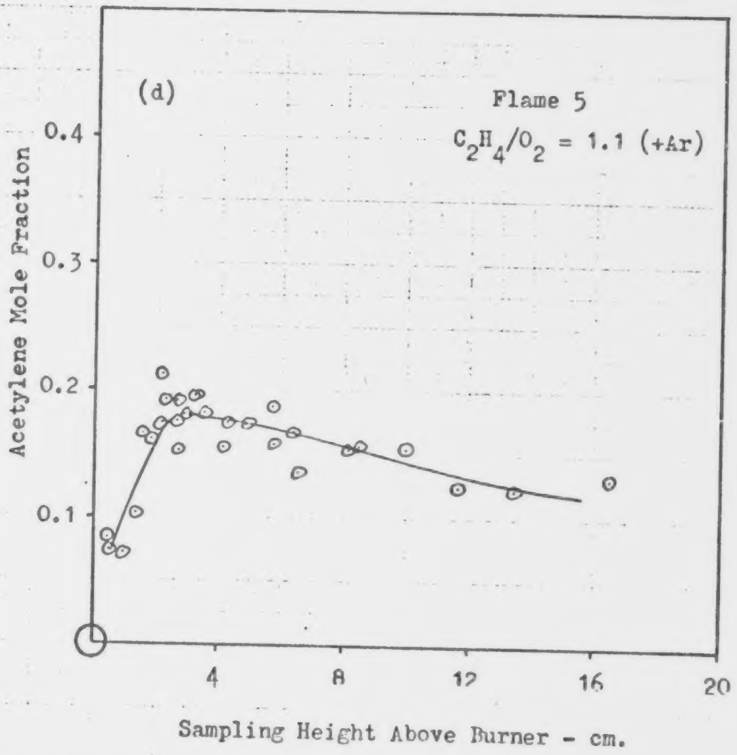


Figure 4.3.4 Ethylene Concentration Profiles
(a)-(b)

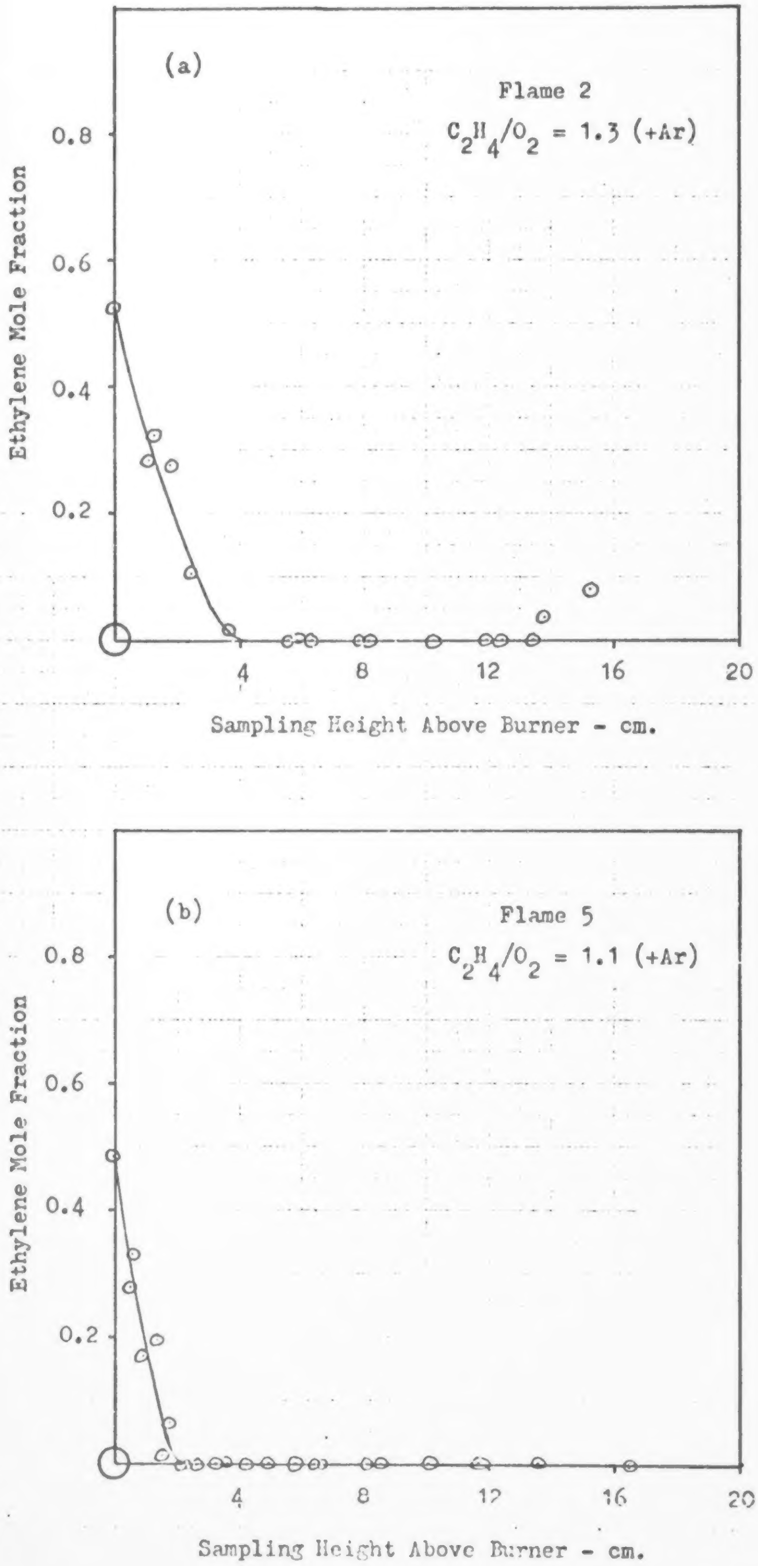


Figure 4.3.5 (a)-(b) (Water + Carbon Monoxide) Concentration Profiles

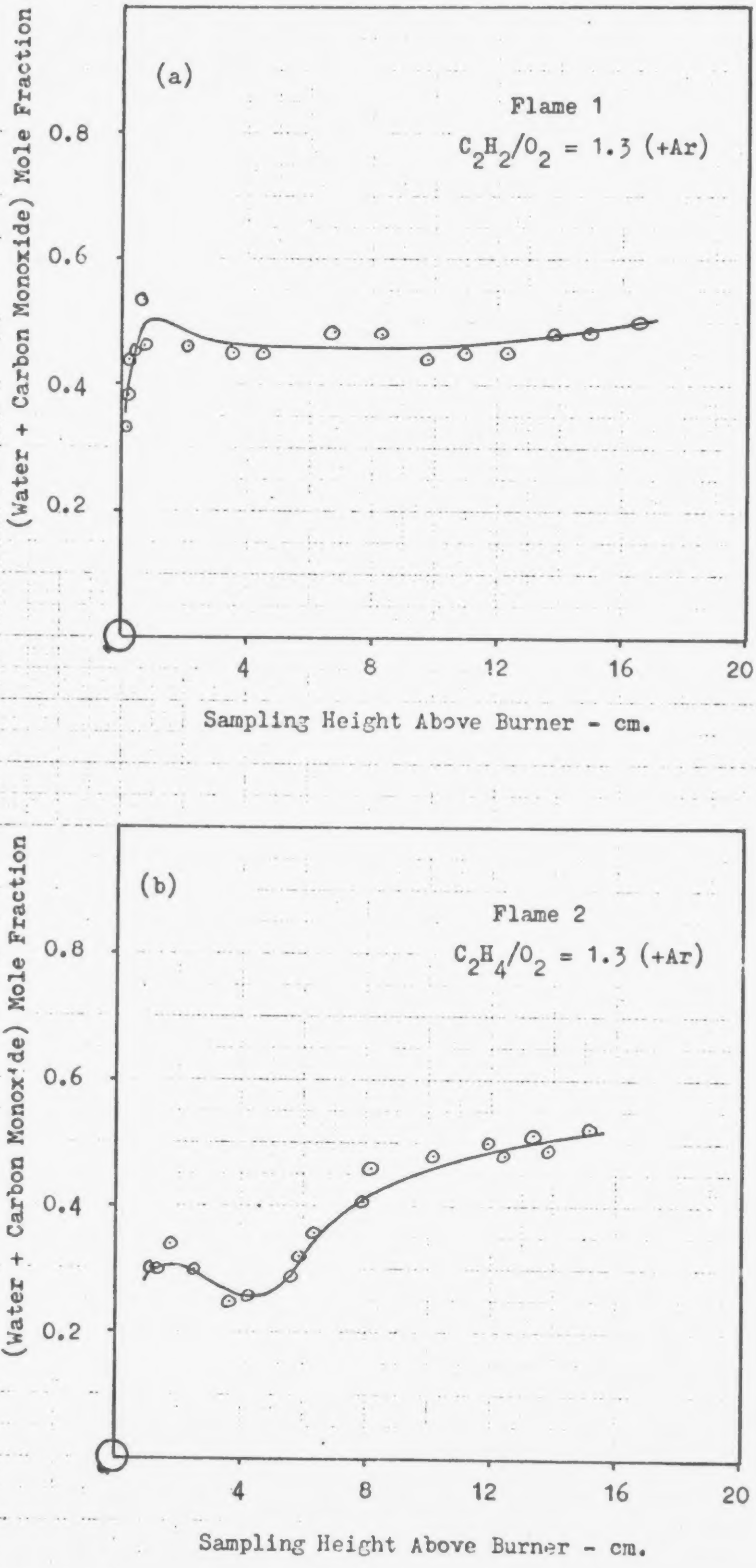


Figure 4.3.5 (c)-(d) (Water + Carbon Monoxide) Concentration Profiles

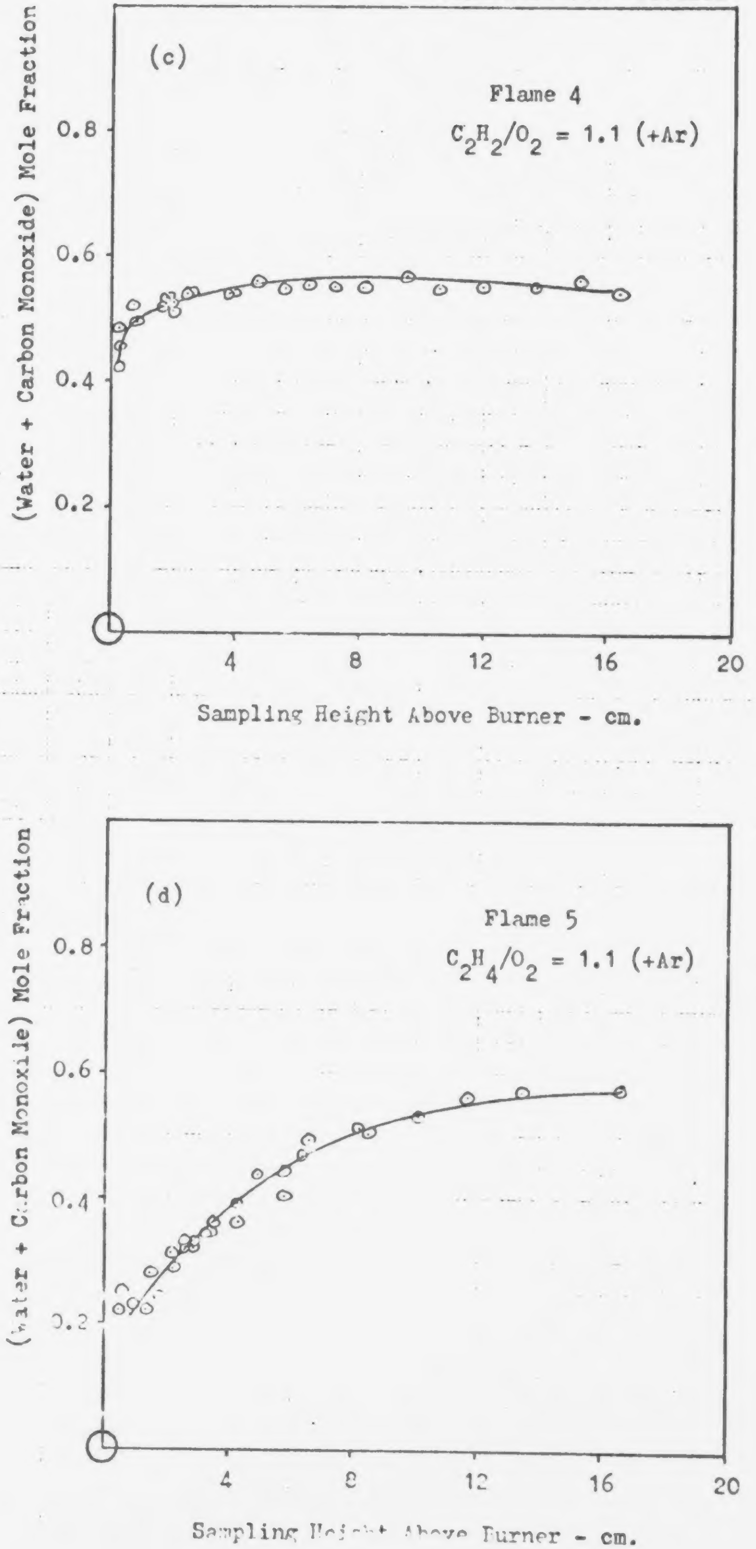
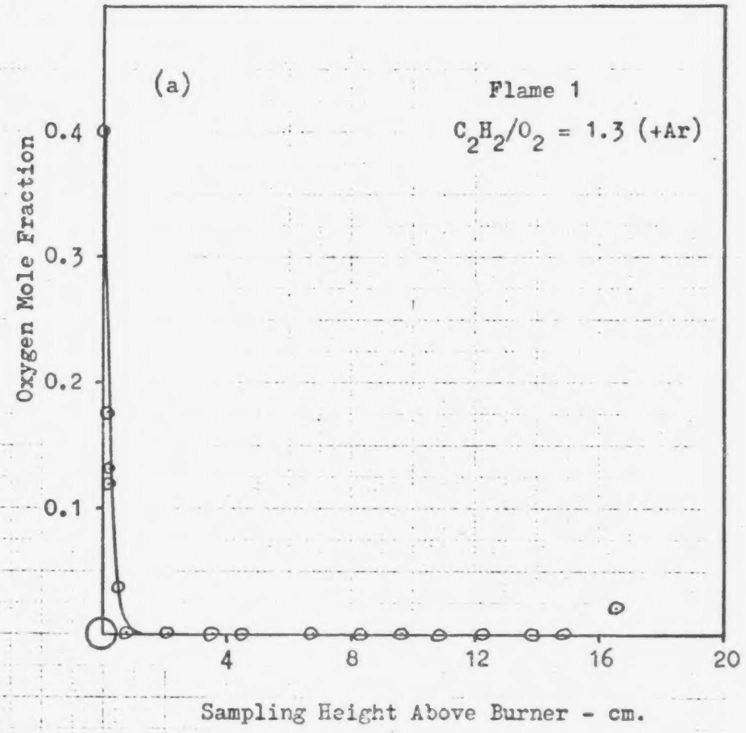


Figure 4.3.6 (a)-(b) Oxygen Concentration Profiles



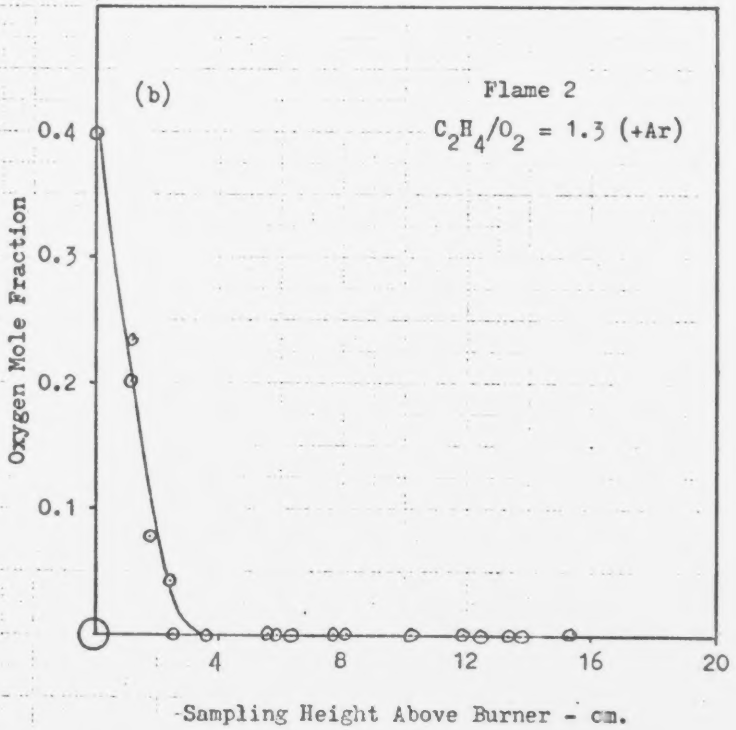


Figure 4.3.6 (c)-(d) Oxygen Concentration Profiles

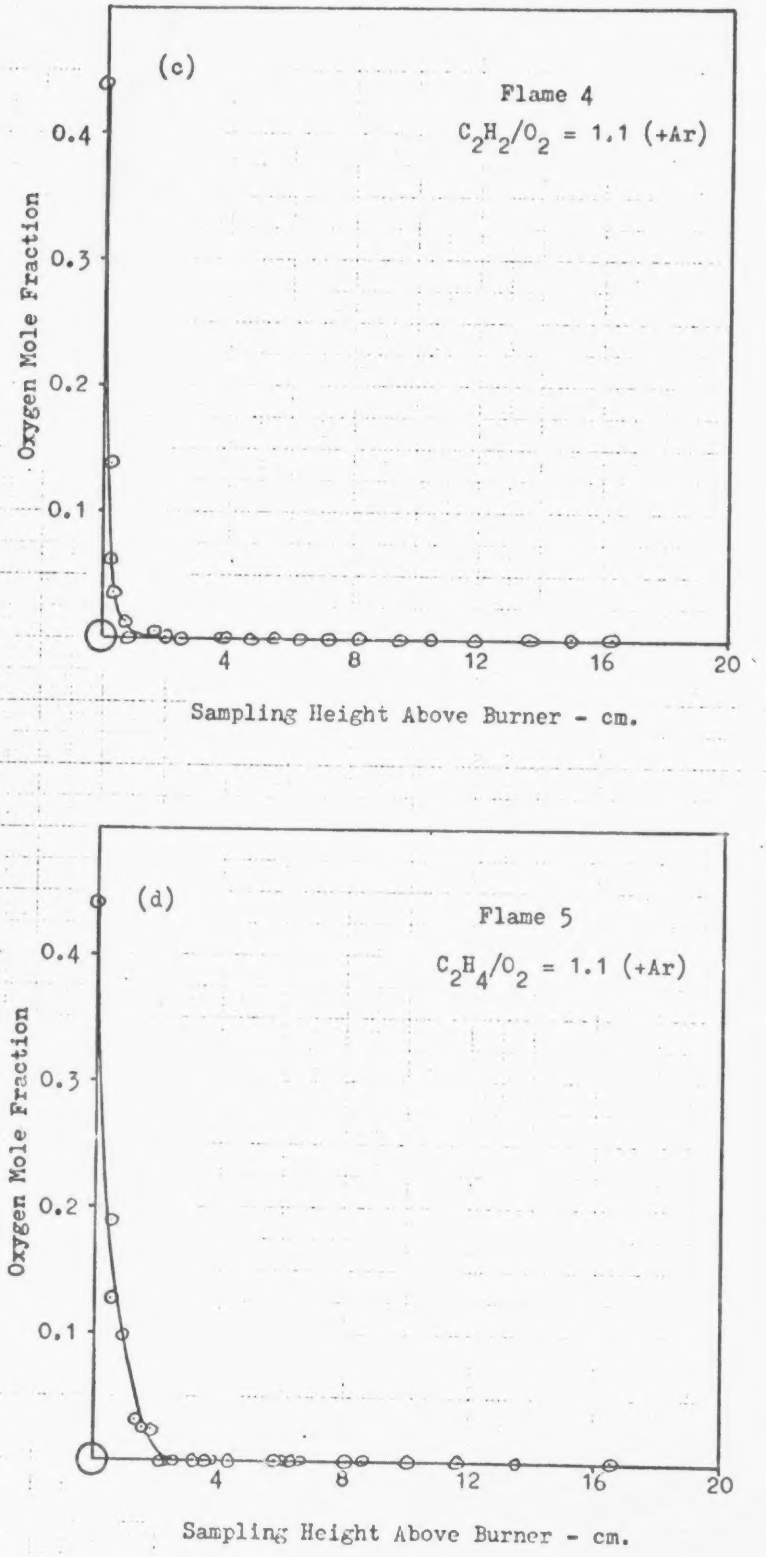


Figure 4.3.7 (a)-(b) Methylacetylene Concentration Profiles

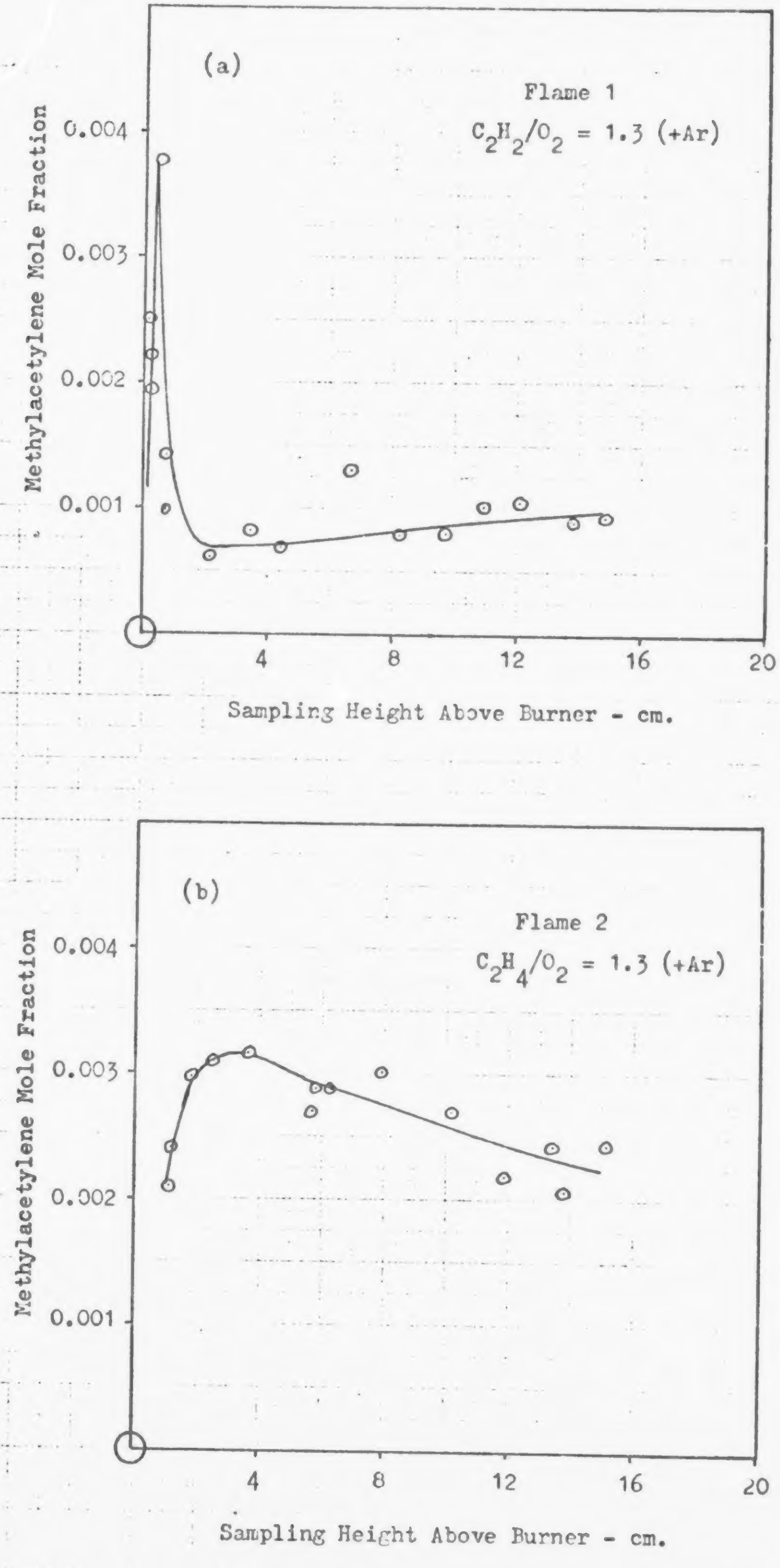
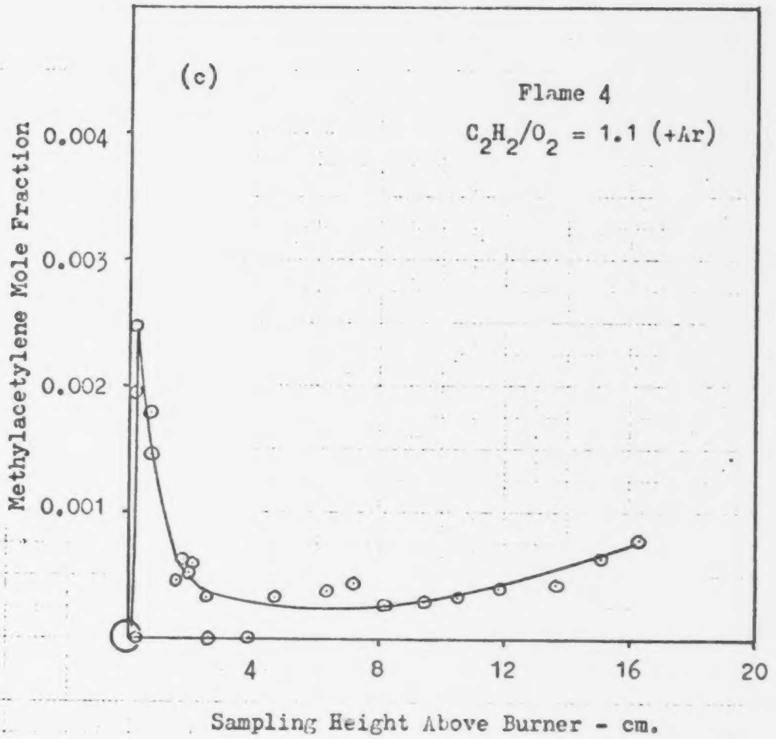


Figure 4.3.7 (c)-(d) Methylacetylene Concentration Profiles



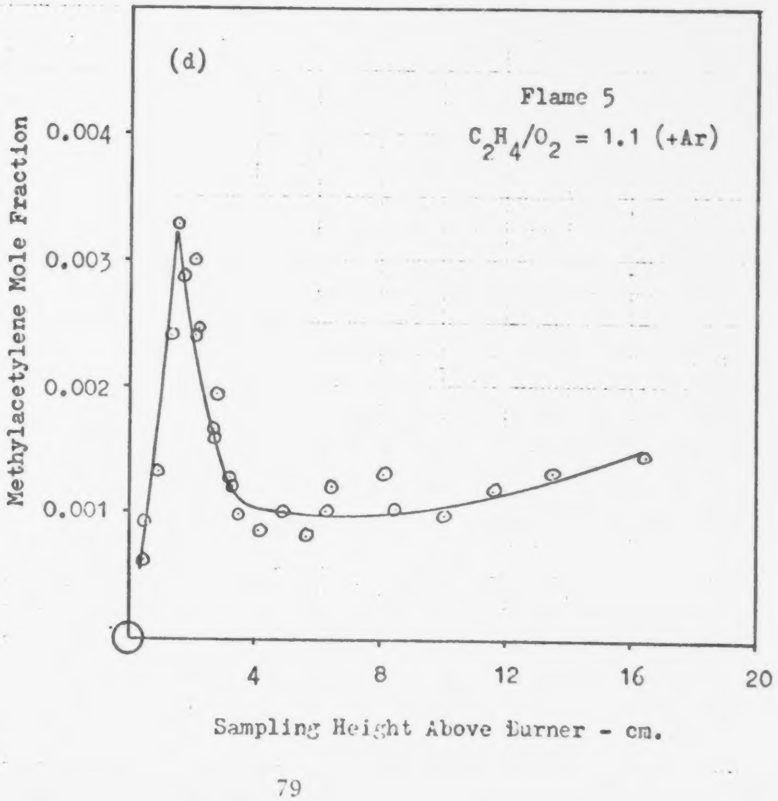
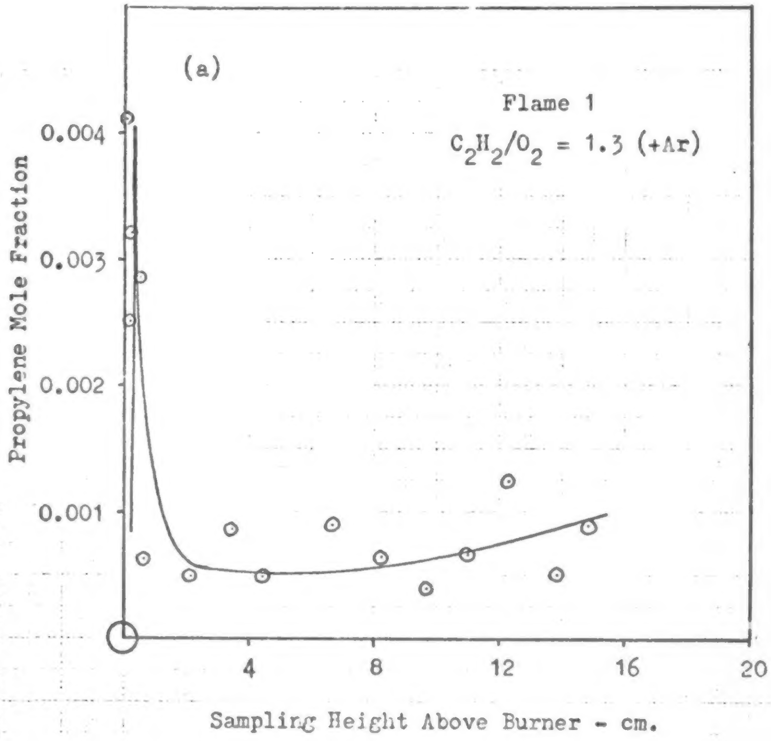


Figure 4.3.8 (a)-(b) Propylene Concentration Profiles



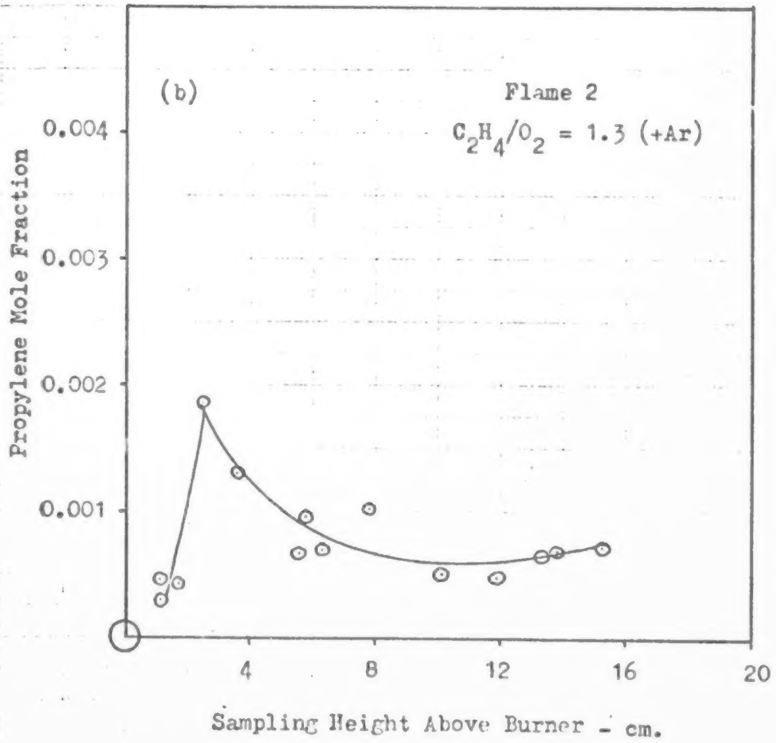


Figure 4.3.8 (c)-(d) Propylene Concentration Profiles

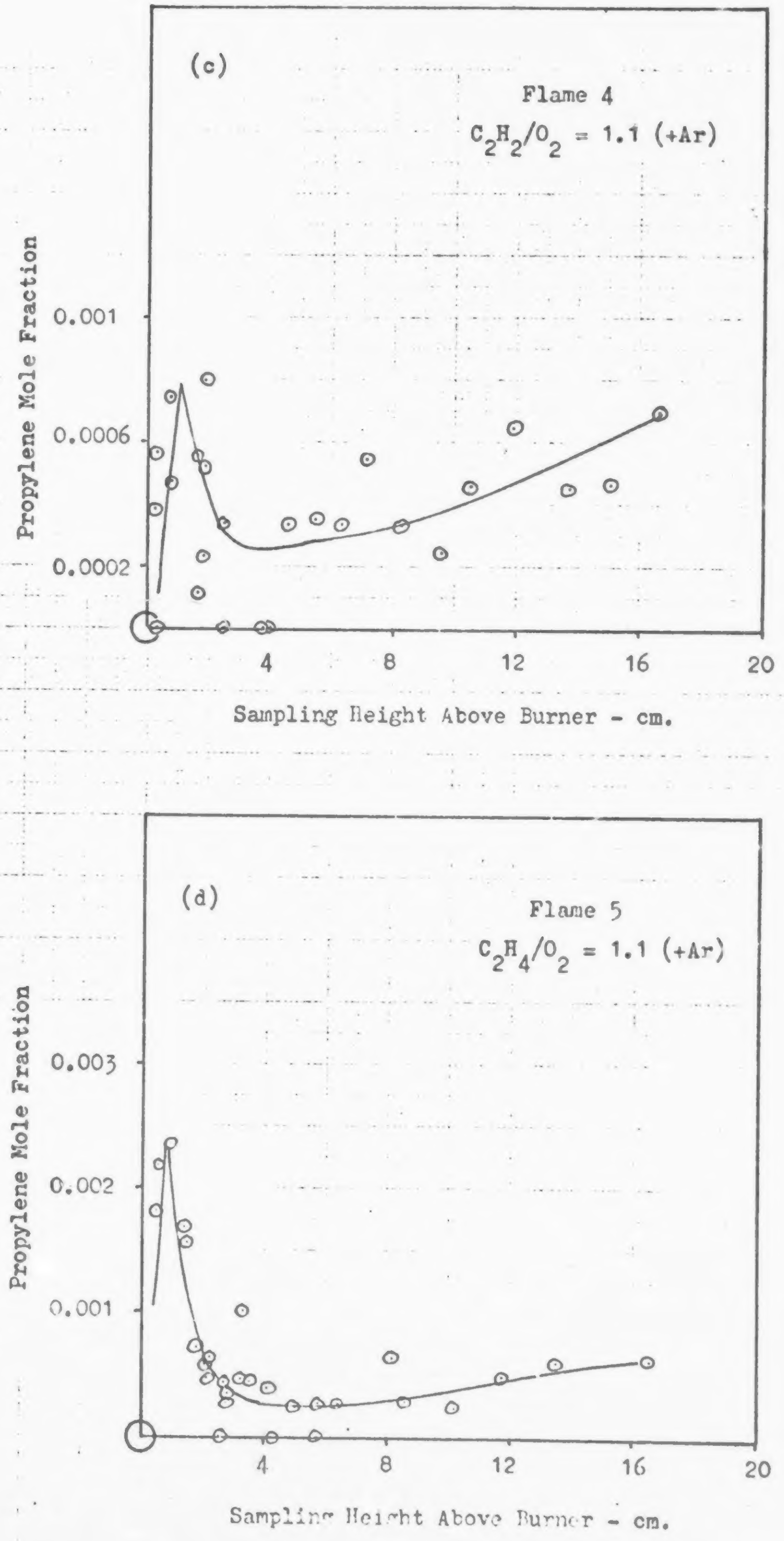


Figure 4.3.9 (a)-(b) Carbon Dioxide Concentration Profiles

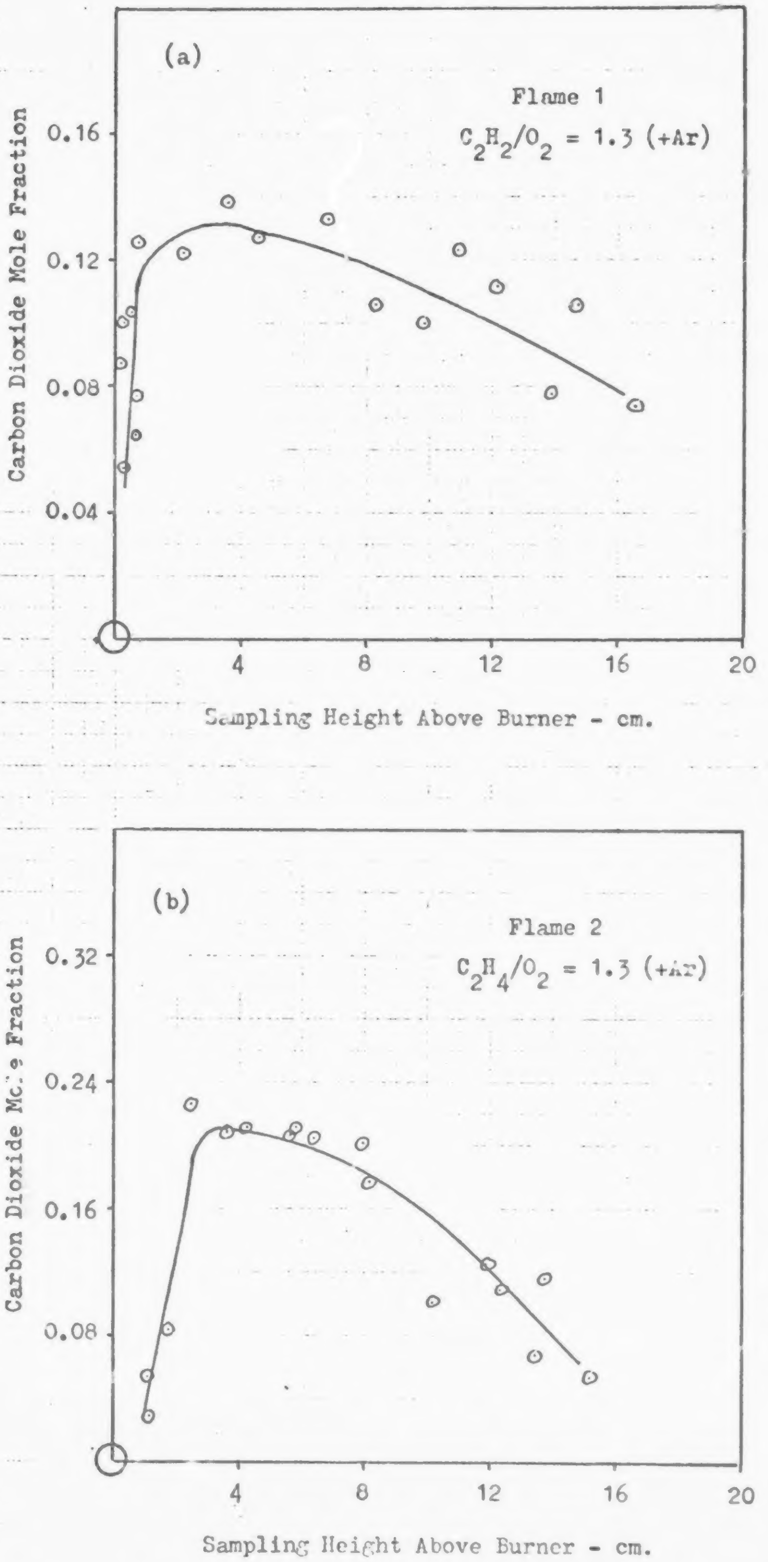


Figure 4.3.9 (c)-(d) Carbon Dioxide Concentration Profiles

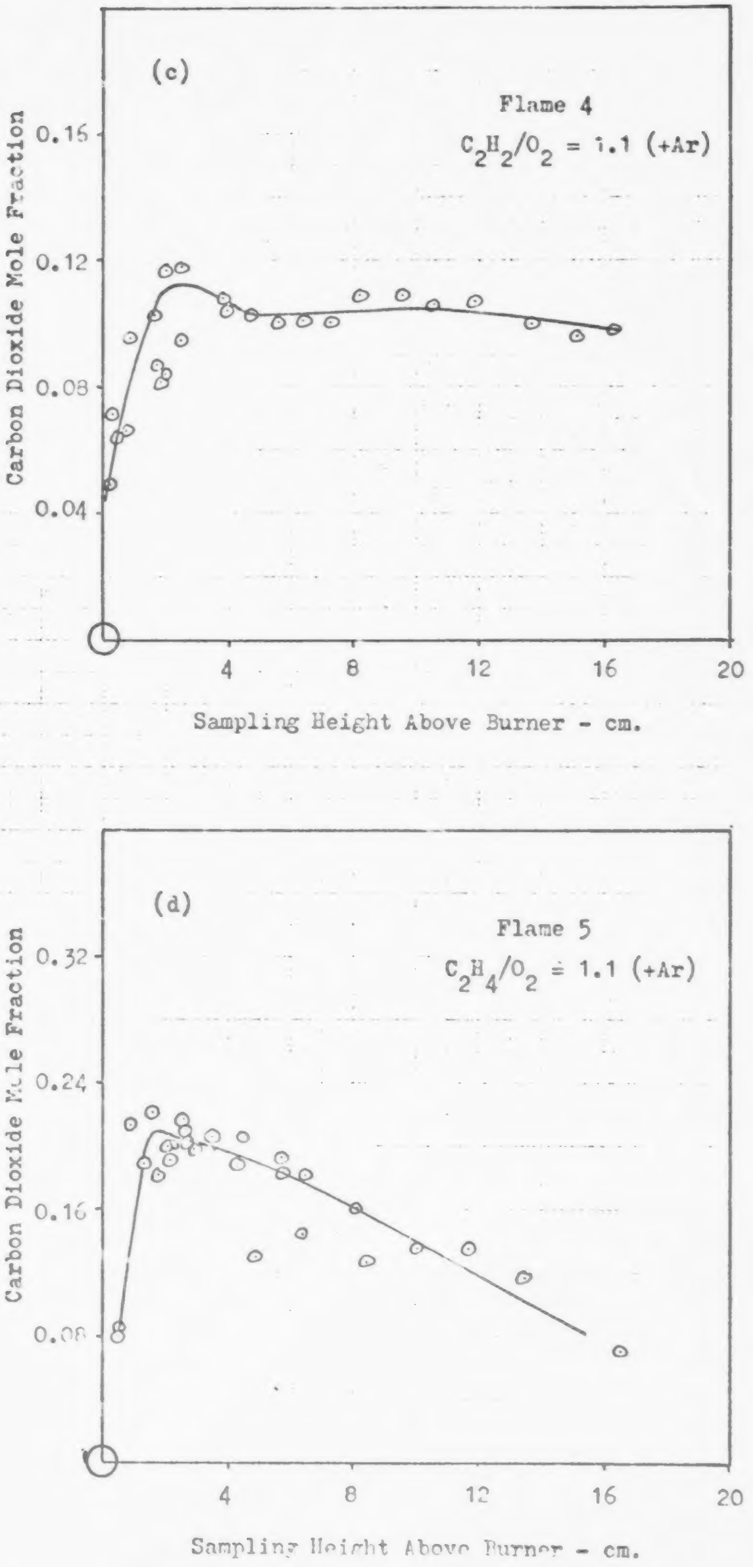


Figure 4.3.10 (a)-(b) Diacetylene Concentration Profiles

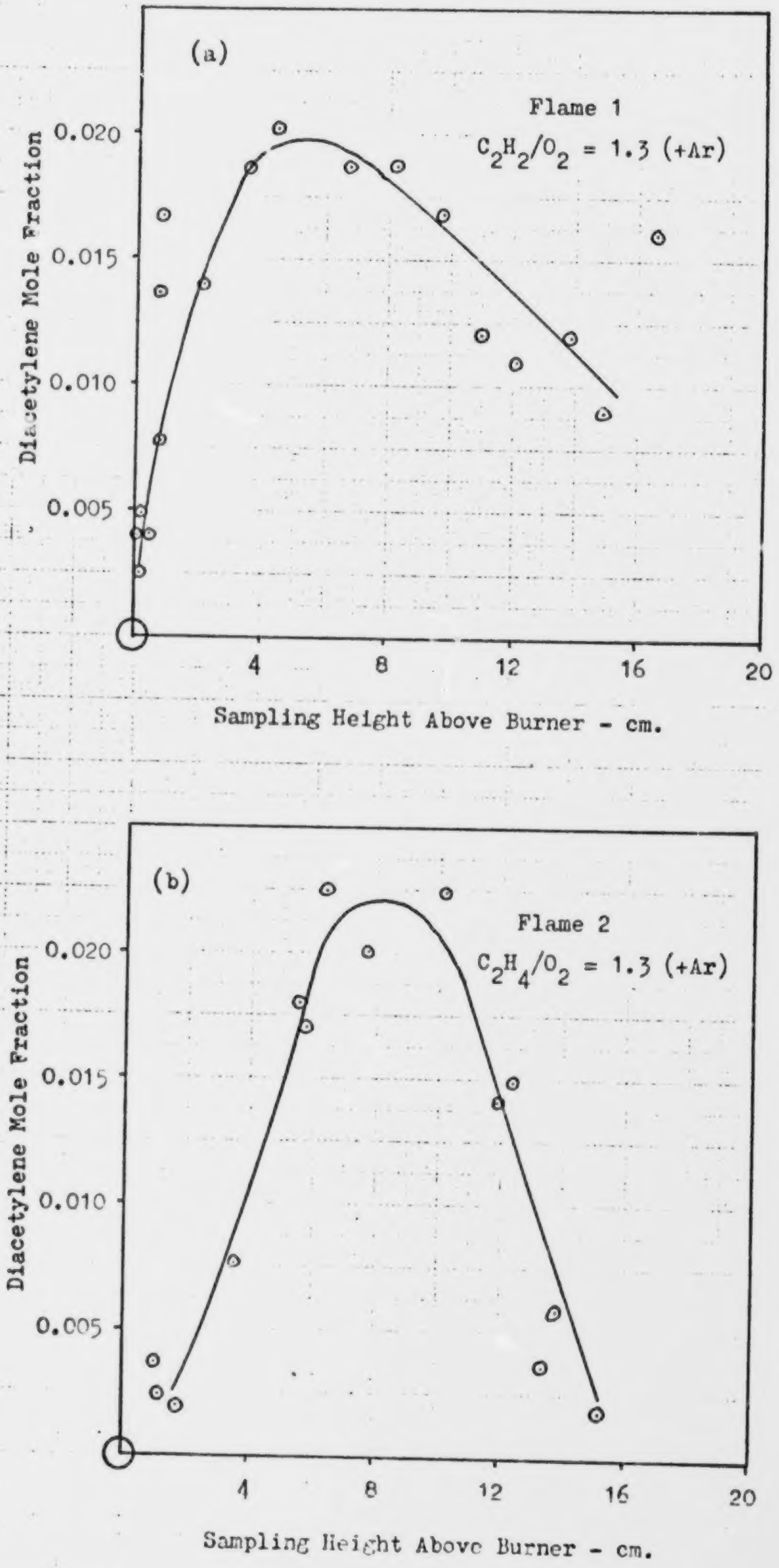


Figure 4.3.10 (c)-(d) Diacetylne Concentration Profiles

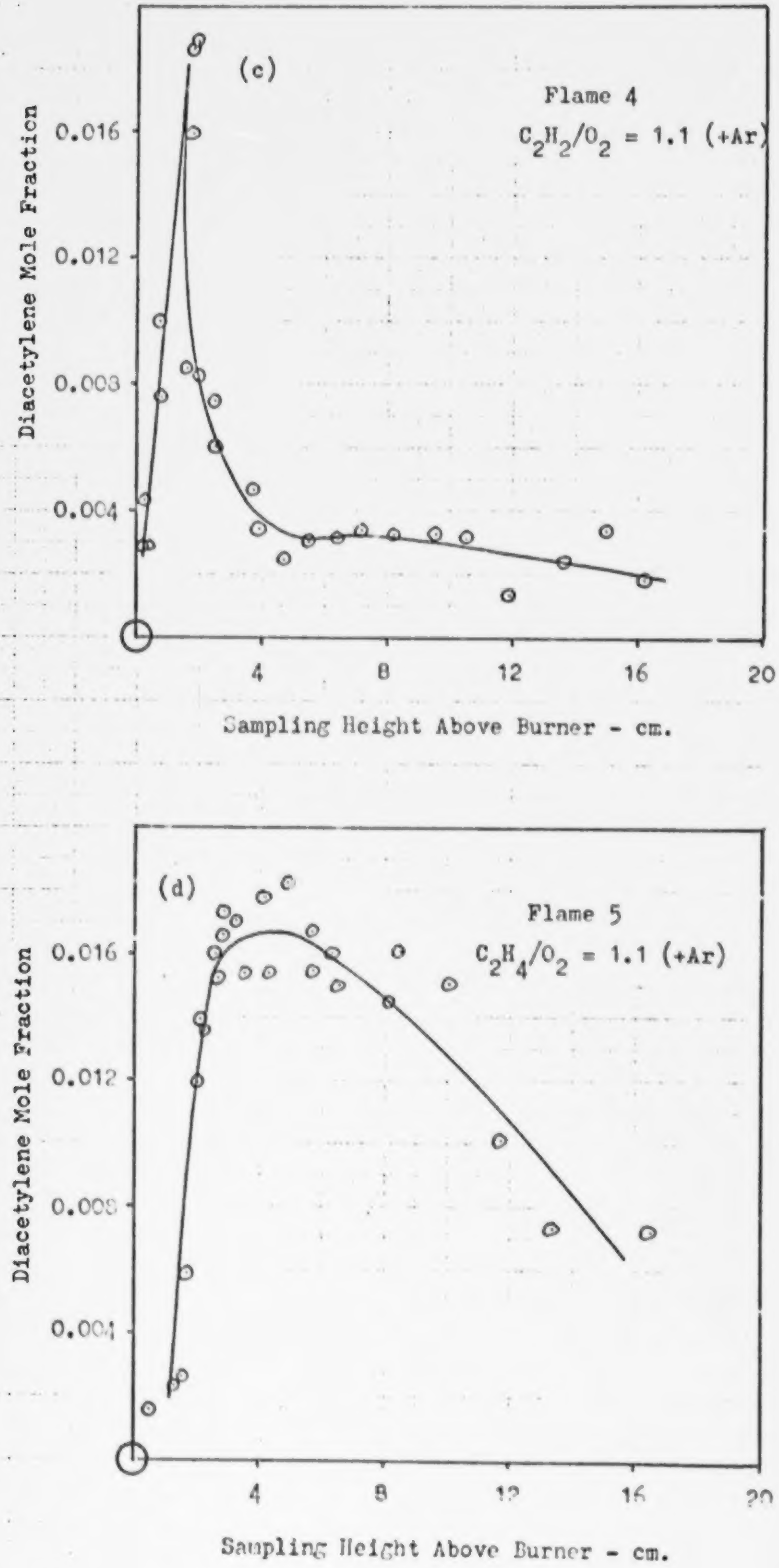
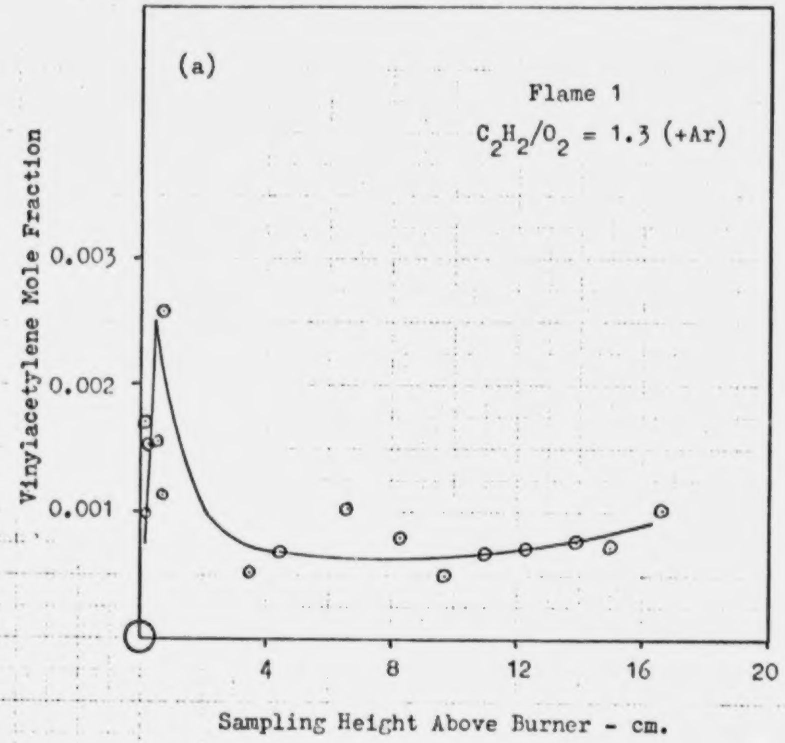


Figure 4.3.11 (a)-(b) Vinylacetylene Concentration Profiles



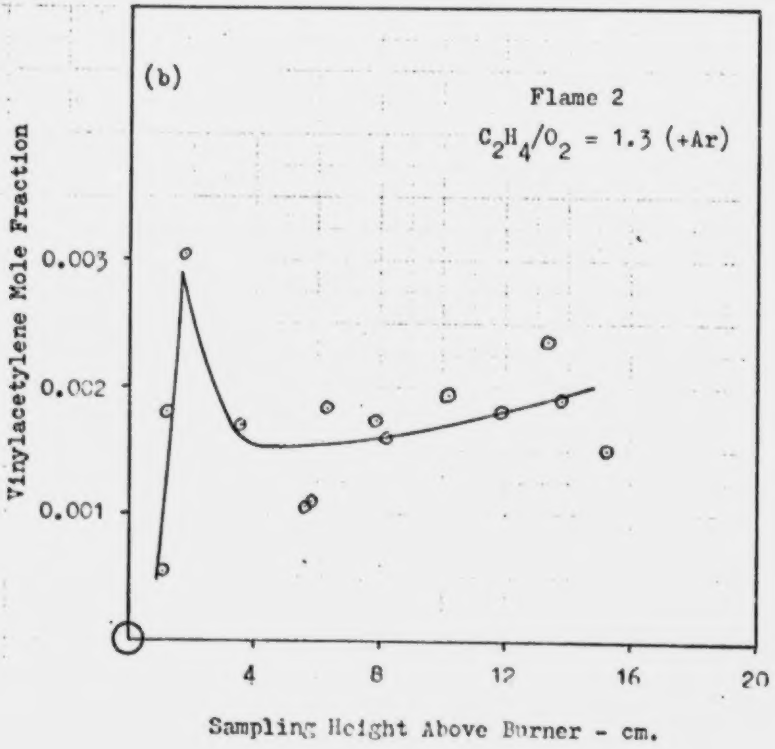
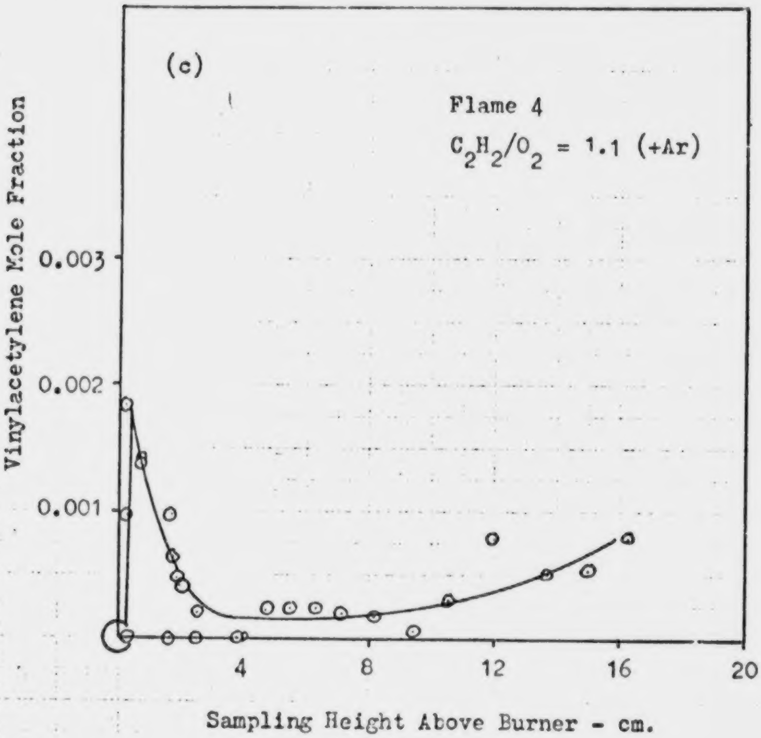


Figure 4.3.11 (c)(d) Vinylacetylene Concentration Profiles



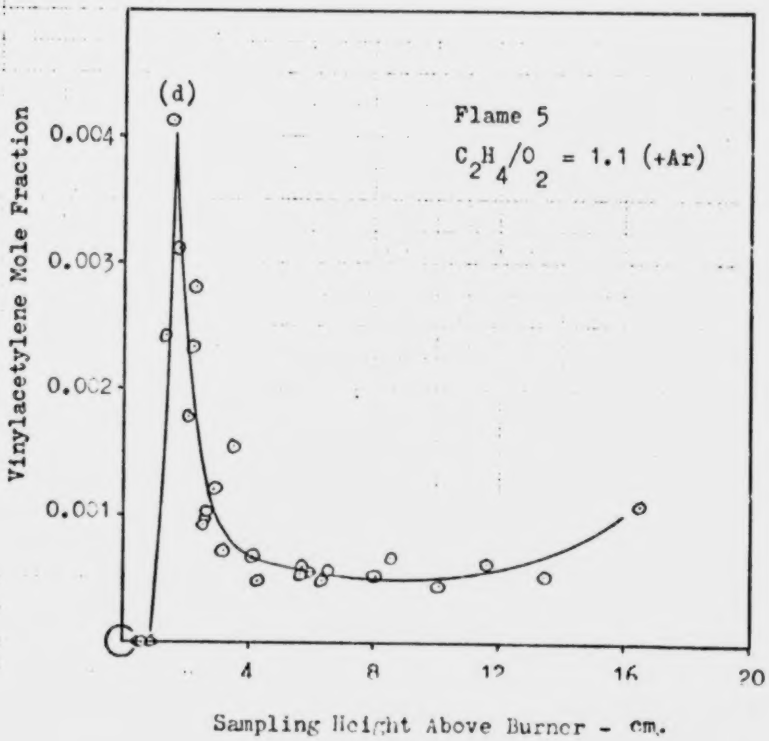


Figure 4.3.12 (a)-(b) Triacetylene Concentration Profiles

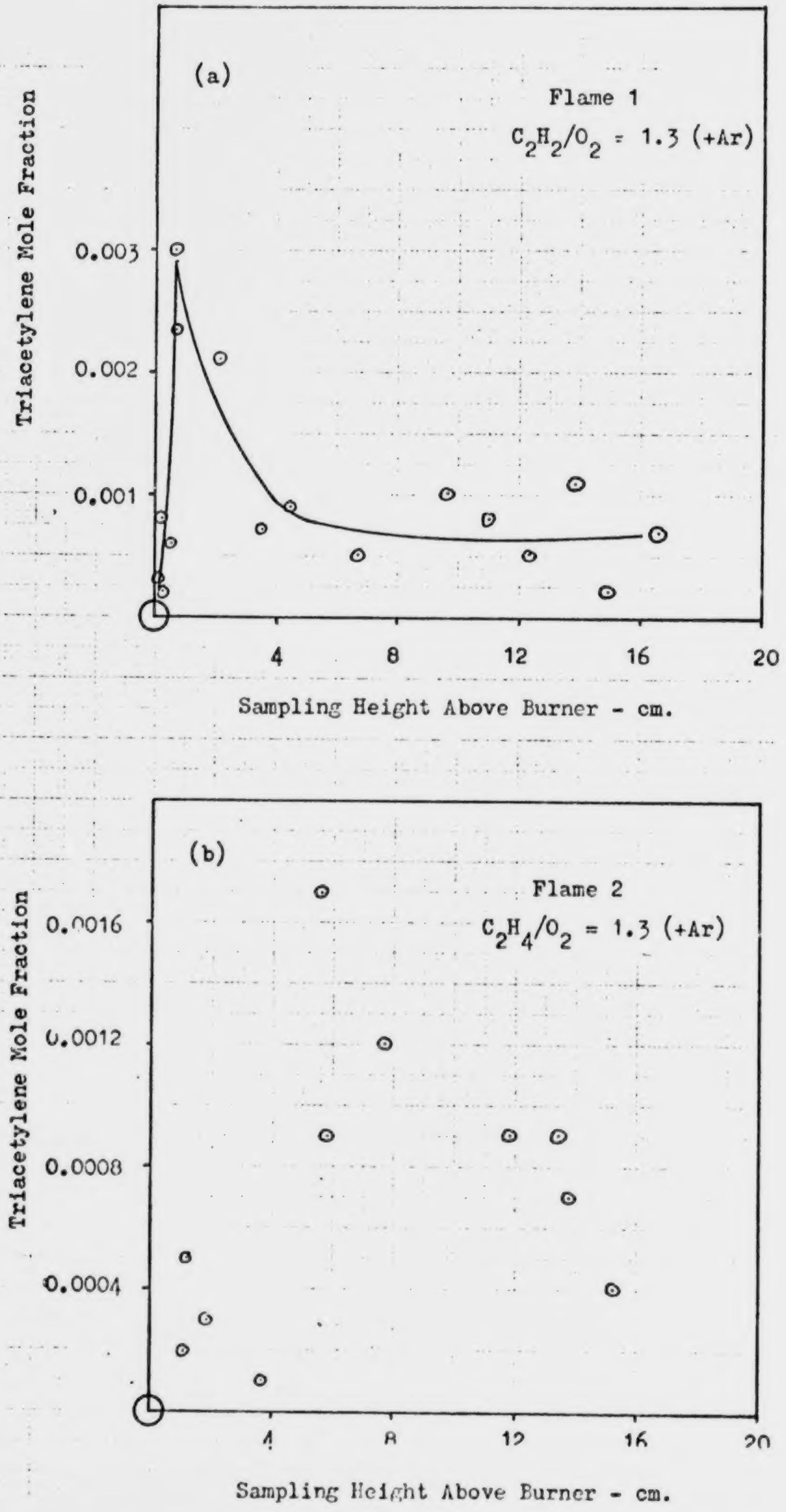


Figure 4.3.12 (c)-(d) Triacetylene Concentration Profiles

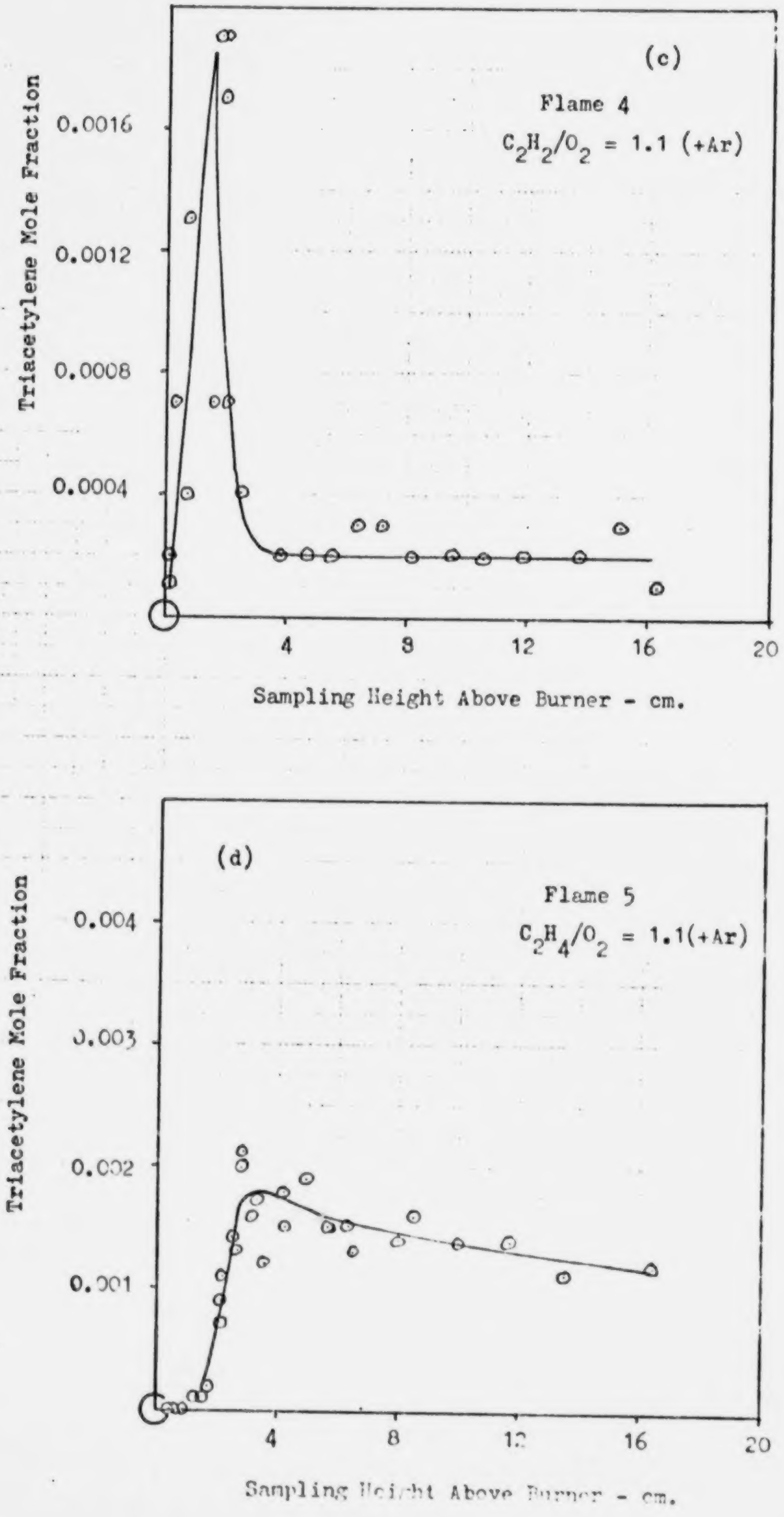
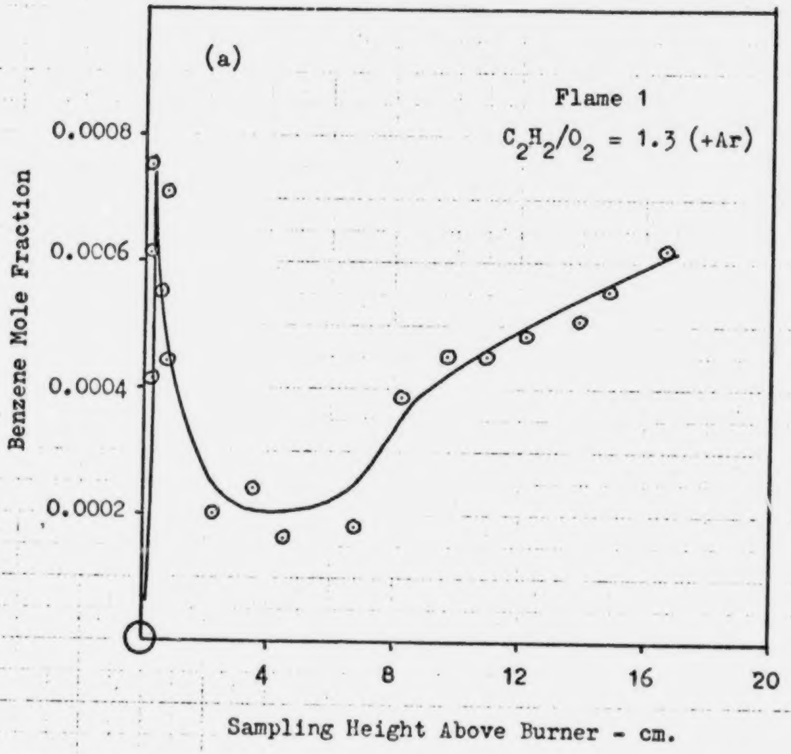


Figure 4.3.13 (a)-(b) Benzene Concentration Profiles



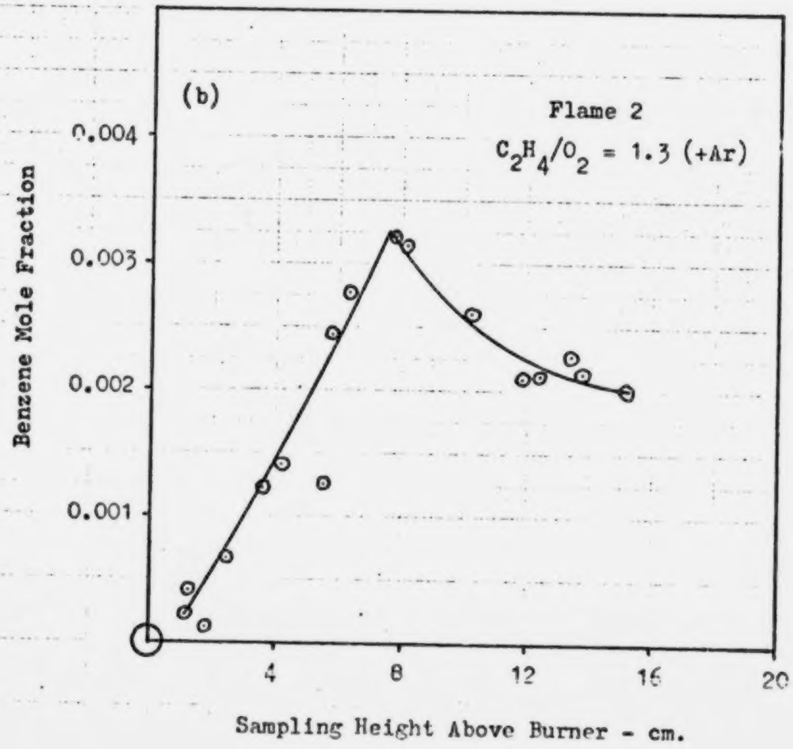


Figure 4.3.13 (c)-(d) Benzene Concentration Profiles

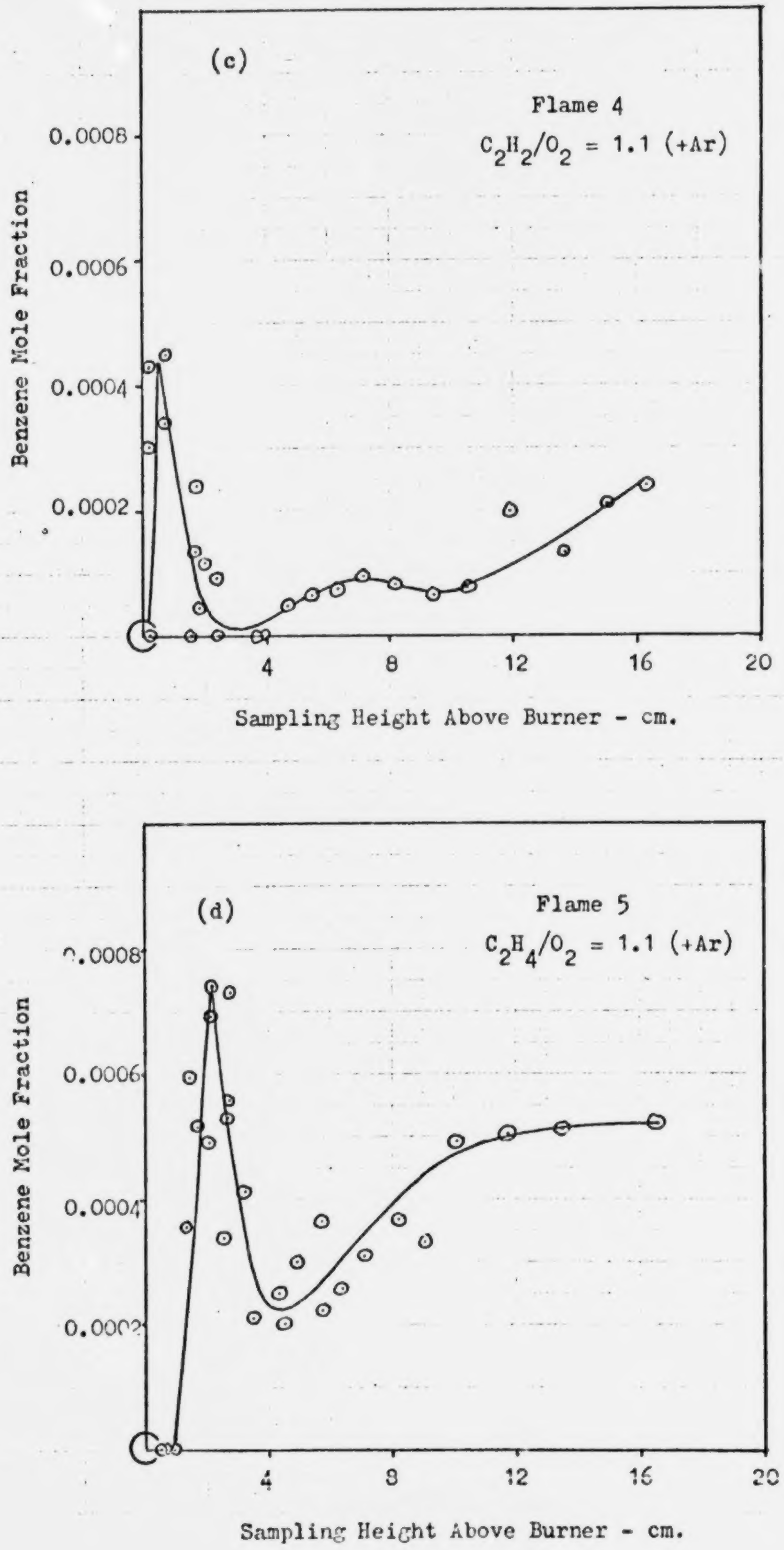


Figure 4.4.1.3.1 (a)-(b) Benzene Concentration Profiles

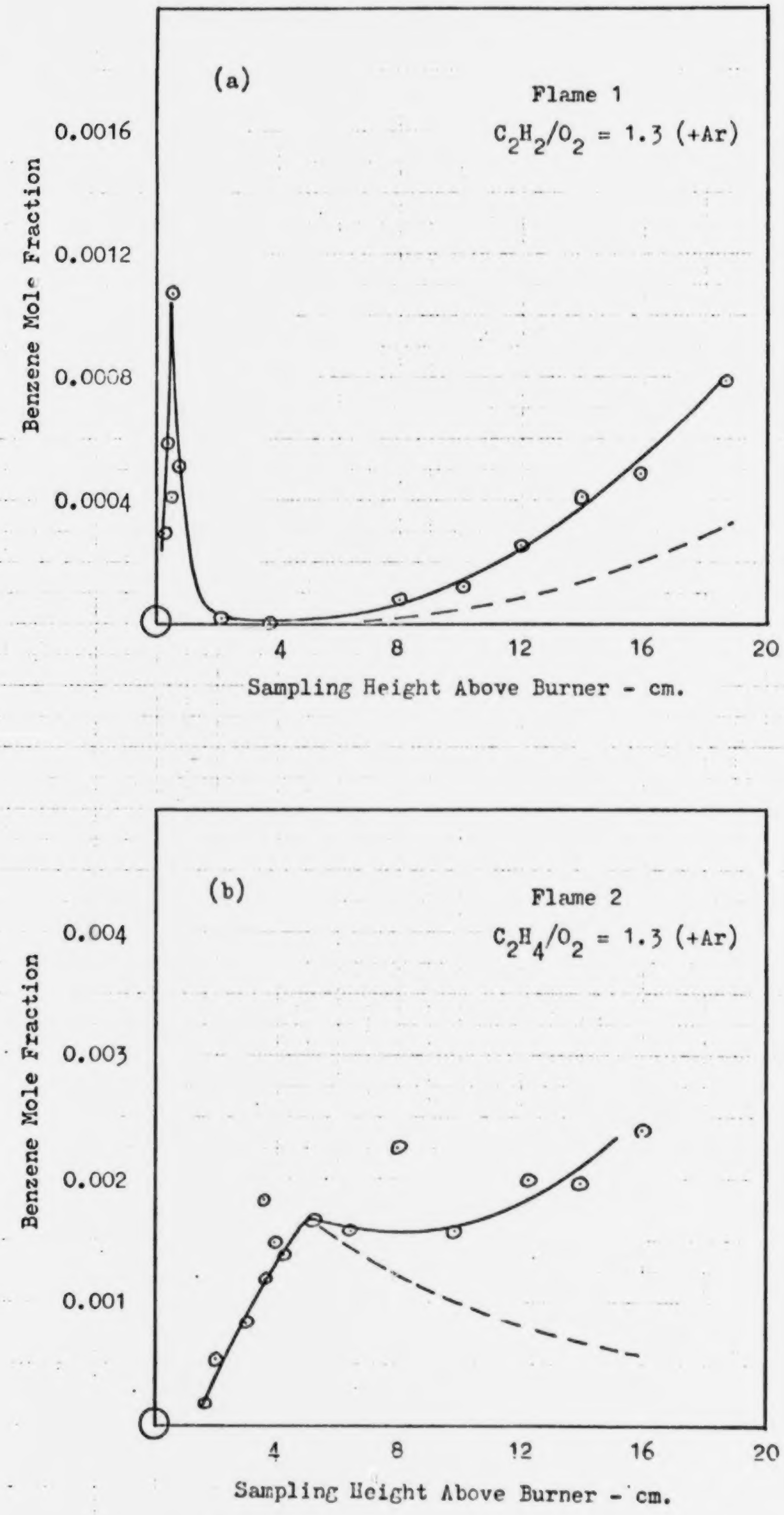


Figure 4.4.1.3.1 (c)-(d) Benzene Concentration Profiles

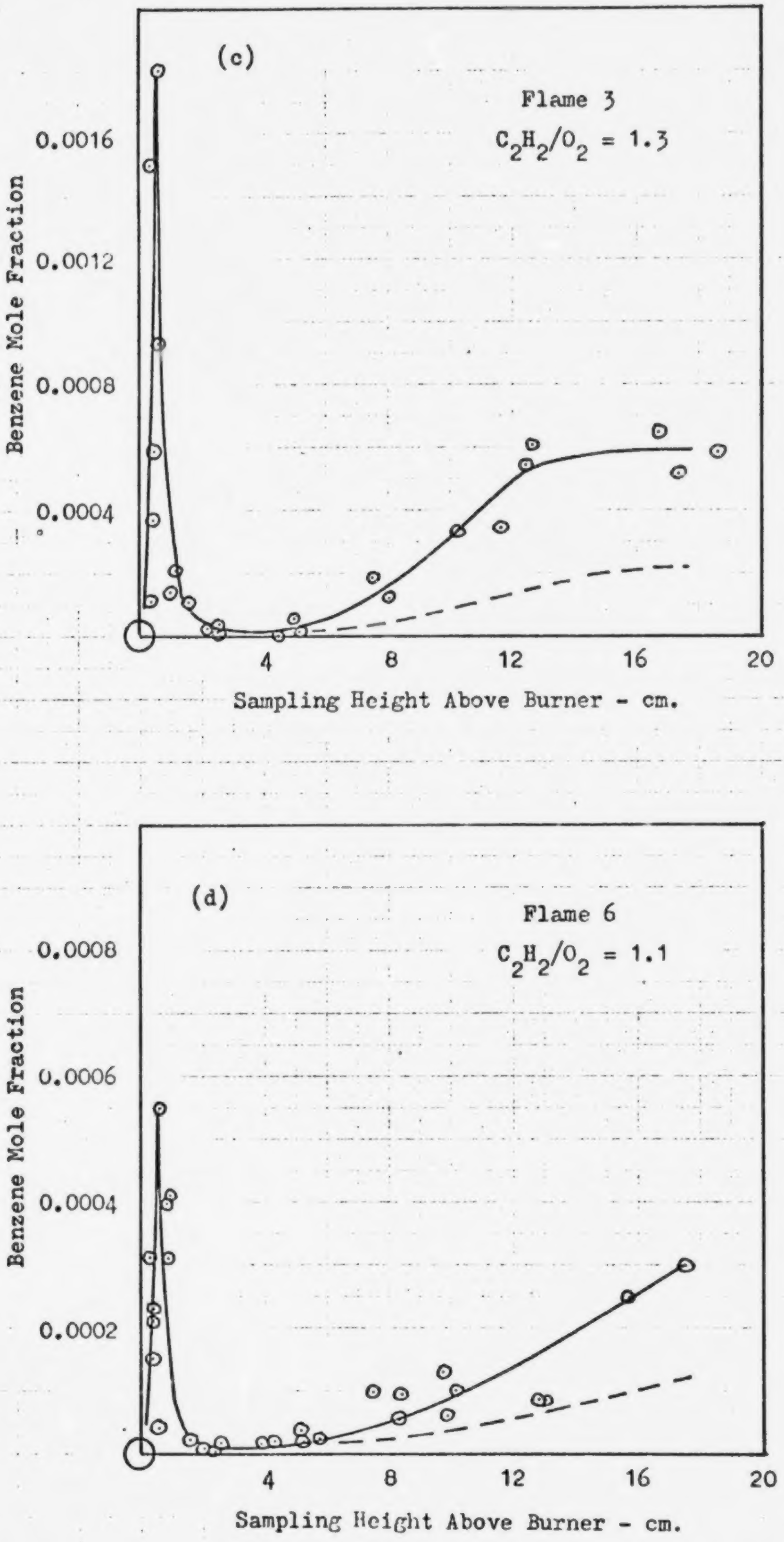


Figure 4.4.1.3.2 (a)-(b) Tetra-acetylene(?) Concentration Profiles

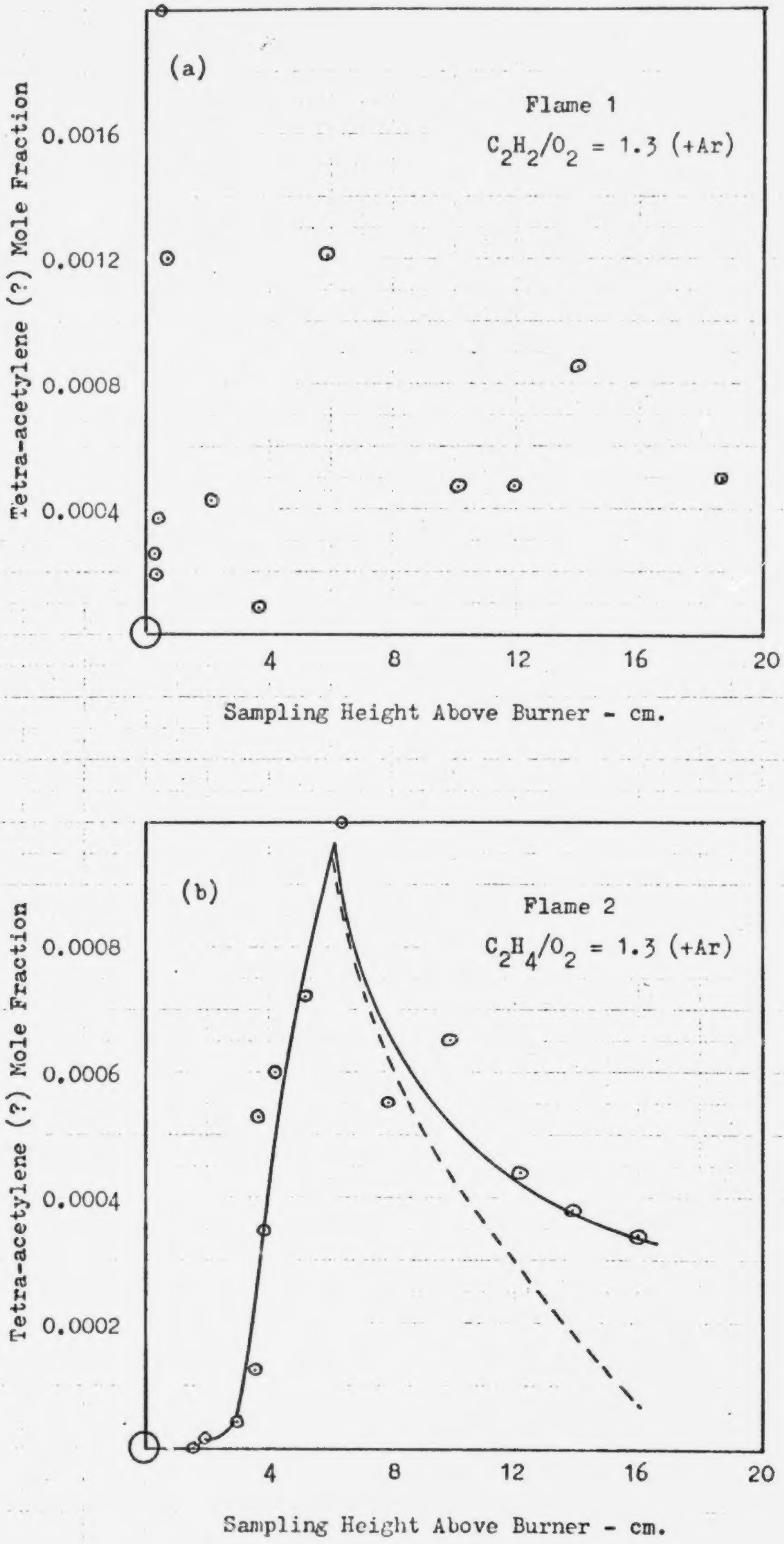


Figure 4.4.1.3.2 (c)-(d) Tetra-acetylene (?) Concentration Profiles

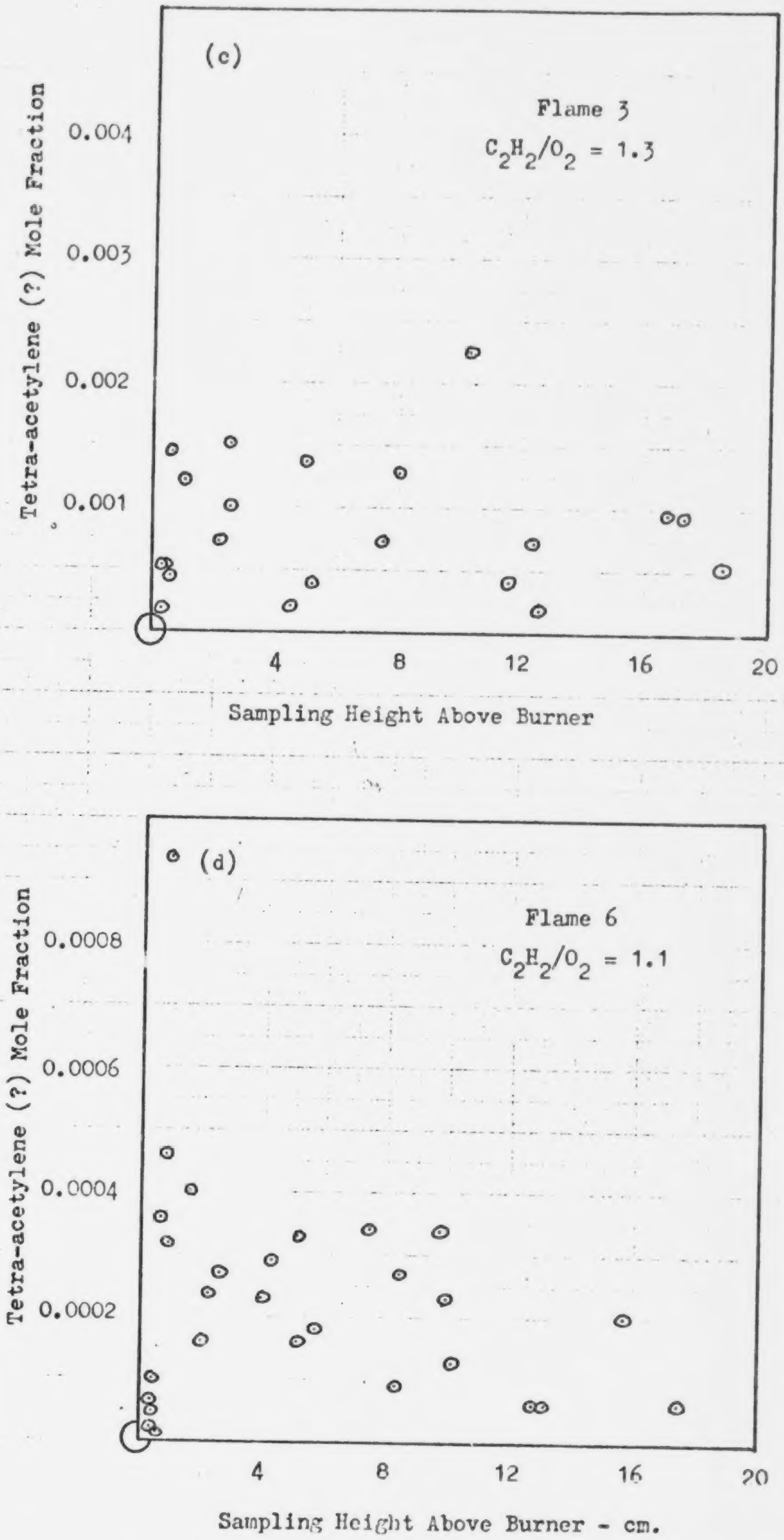


Figure 4.4.1.3.3 (a)-(b) Toluene Concentration Profiles

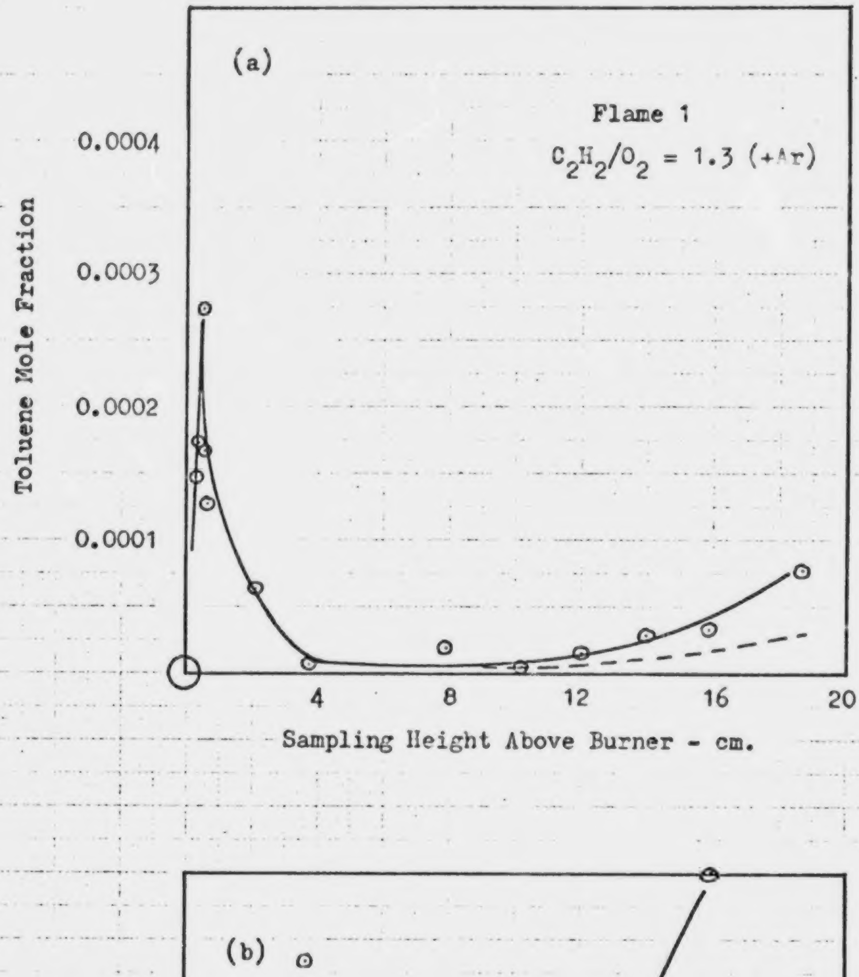
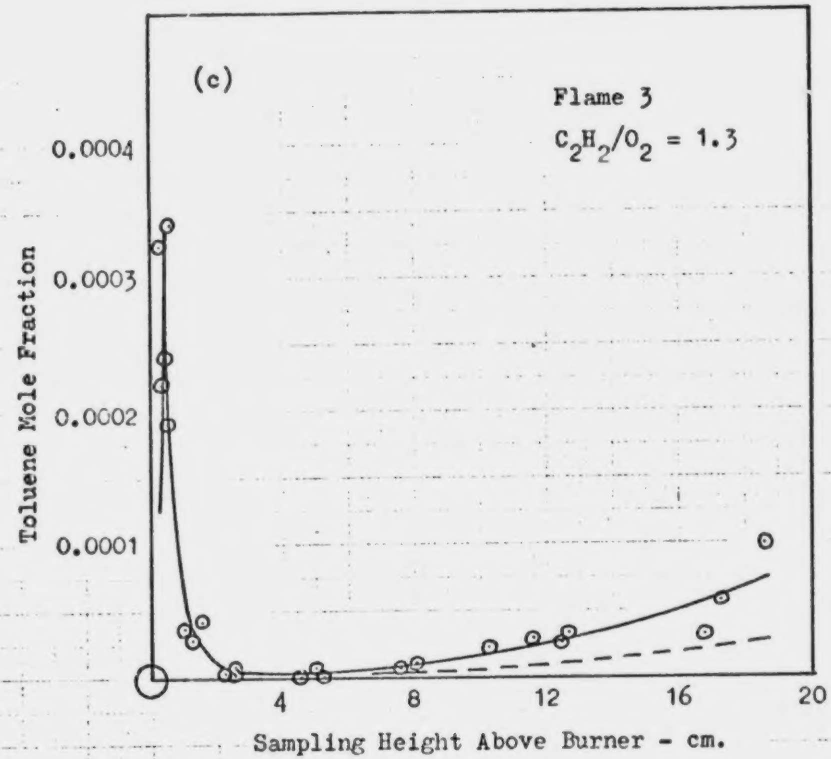

(a)
Flame 1
C_2H_2/O_2 = 1.3 (+Ar)
Toluene Mole Fraction
0.0004
0.0003
0.0002
0.0001
4
8
12
16
20
Sampling Height Above Burner - cm.
(b)
0.00016
0.00012
0.00008
0.00004
Toluene Mole Fraction
Flame 2
C_2H_4/O_2 = 1.3 (+Ar)
4
8
12
16
20
Sampling Height Above Burner - cm.

Figure 4.4.1.3.3 (c)-(d) Toluene Concentration Profiles



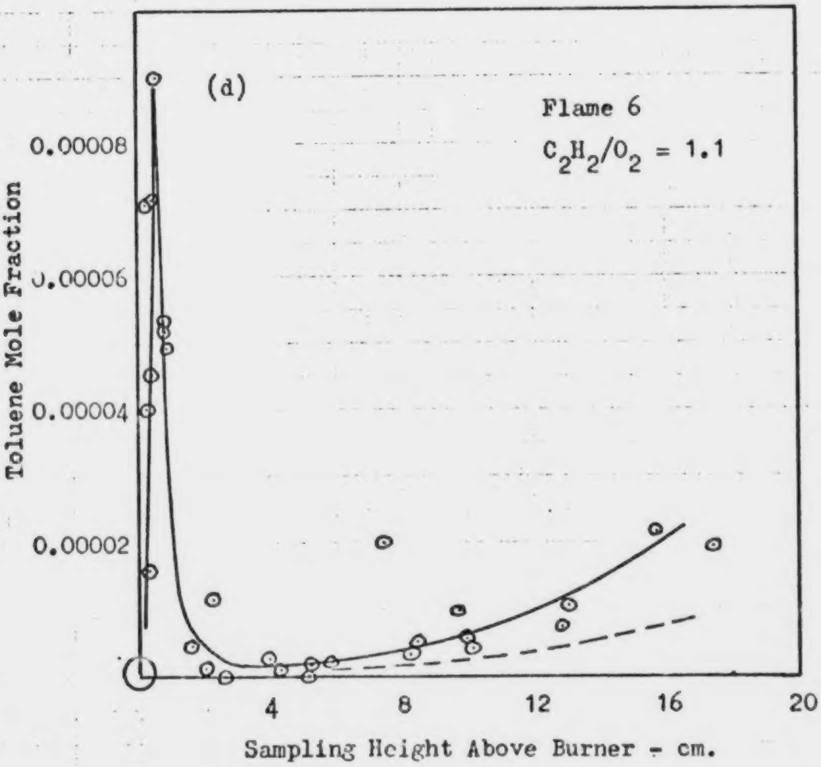


Figure 4.4.1.3.4 (a)-(b) Phenylacetylene Concentration Profiles

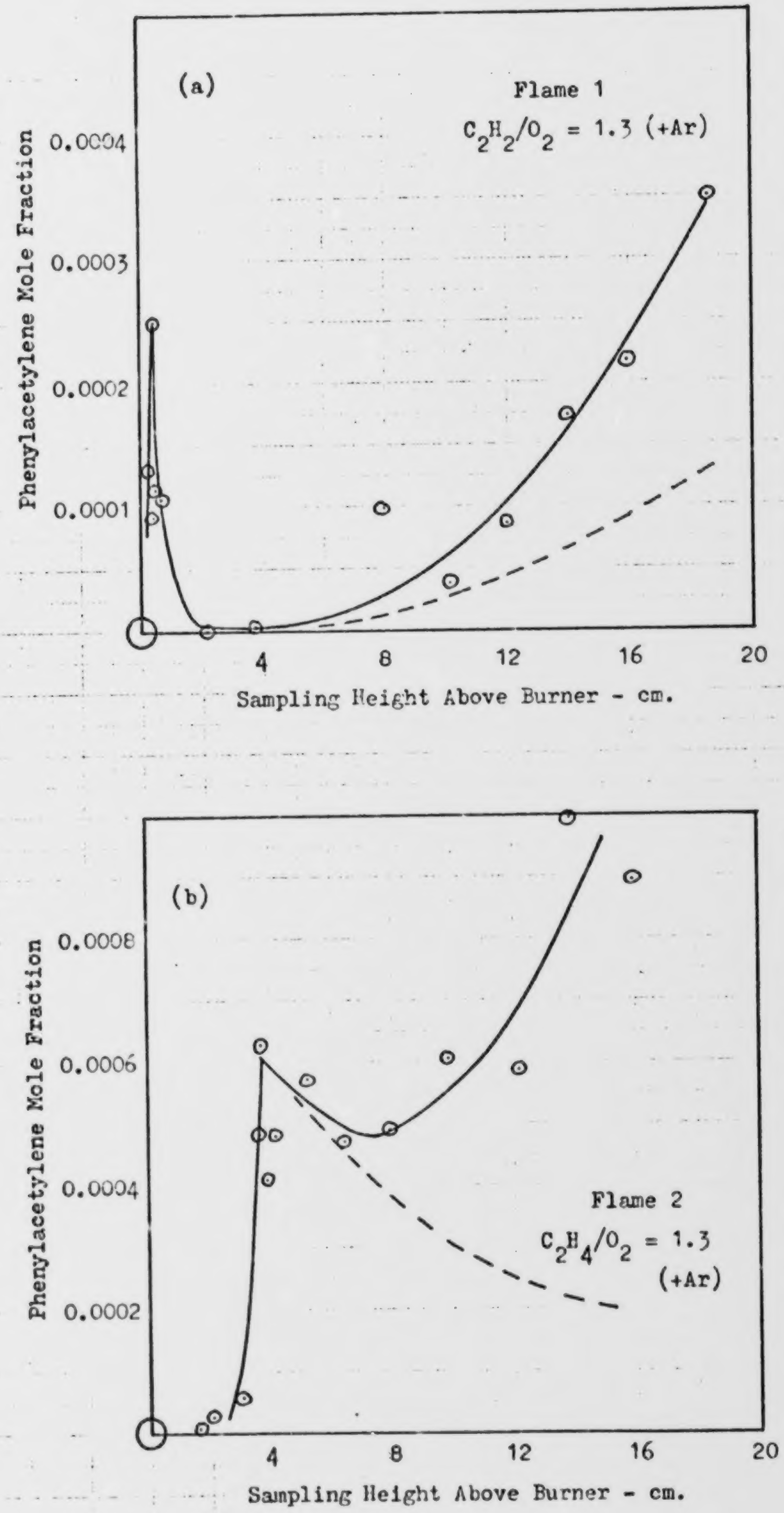
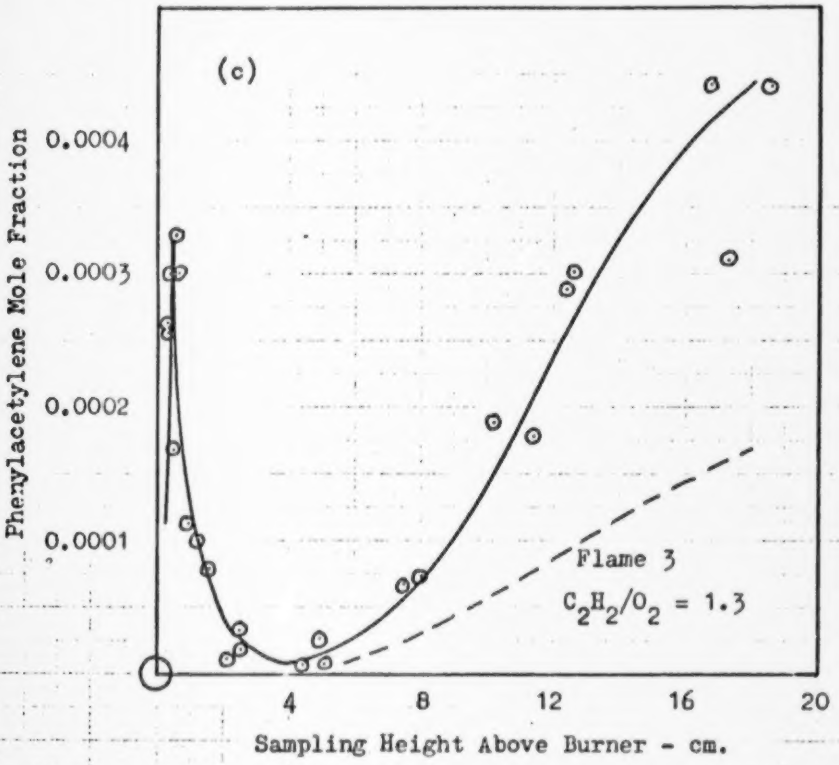


Figure 4.4.1.3.4 (c)-(d) Phenylacetylene Concentration Profiles



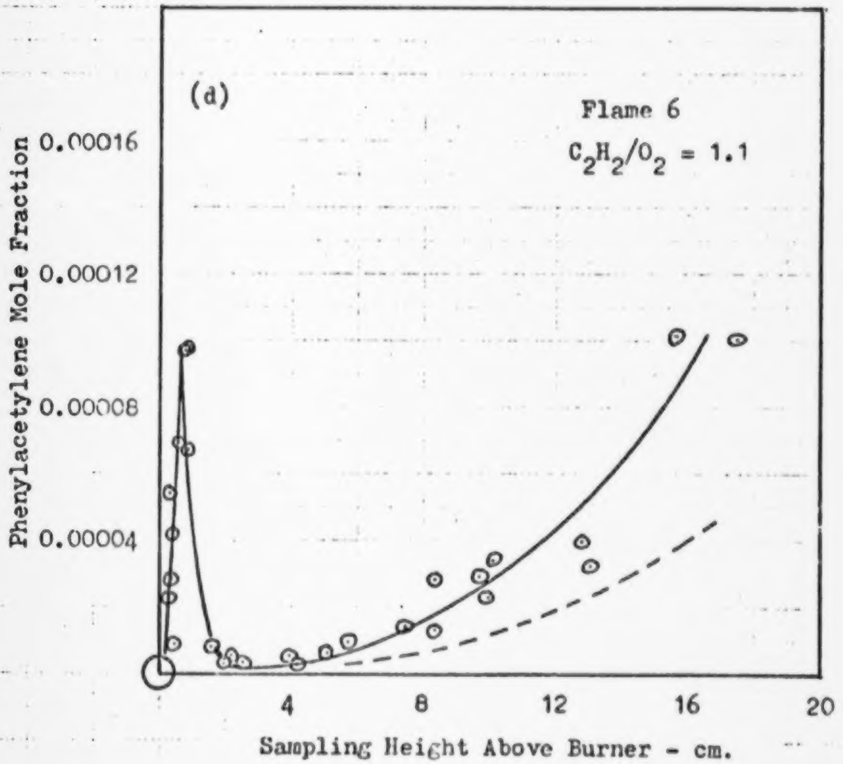


Figure 4.4.1.3.5 Styrene Concentration Profiles
(a)-(b)

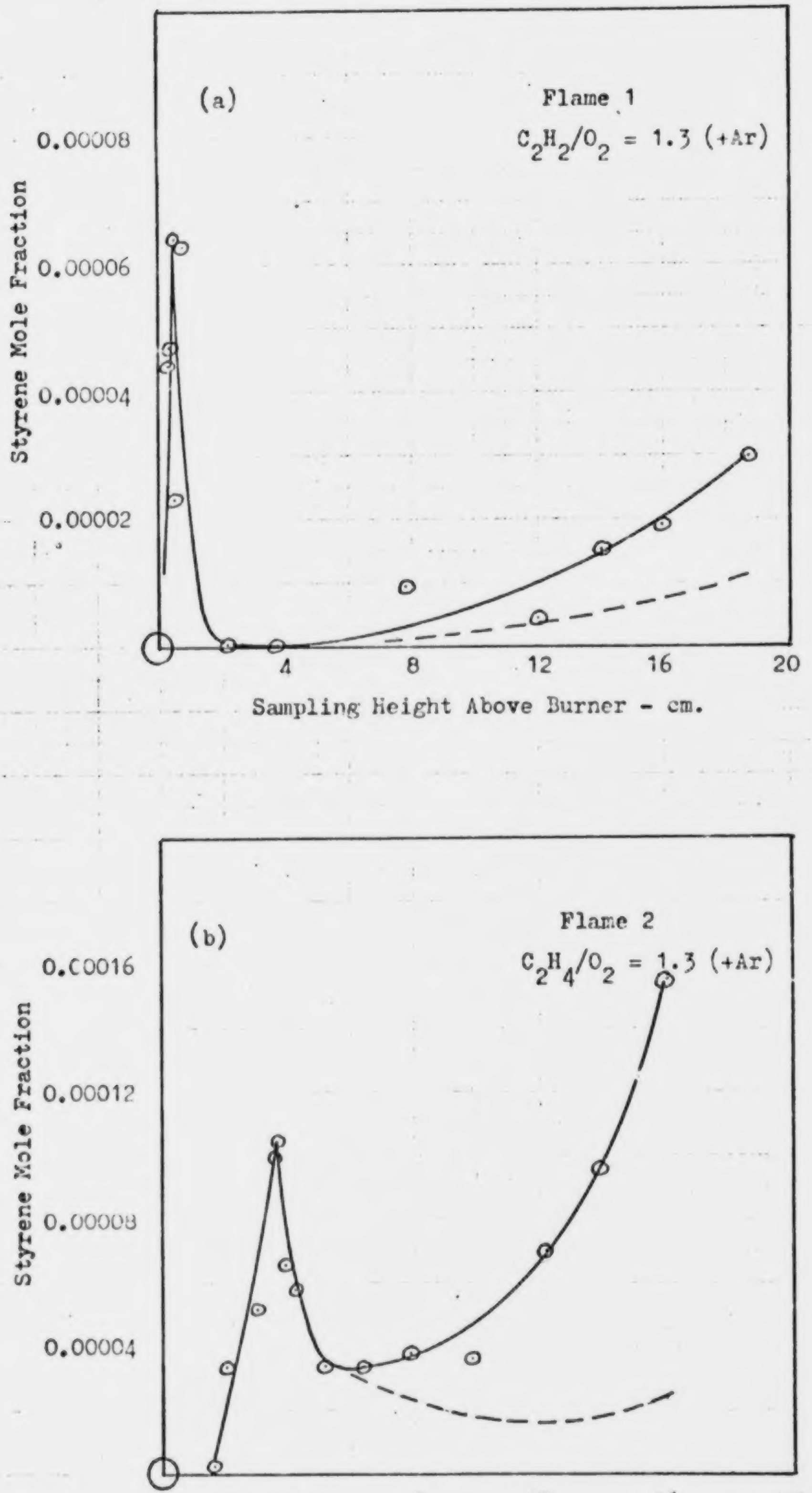
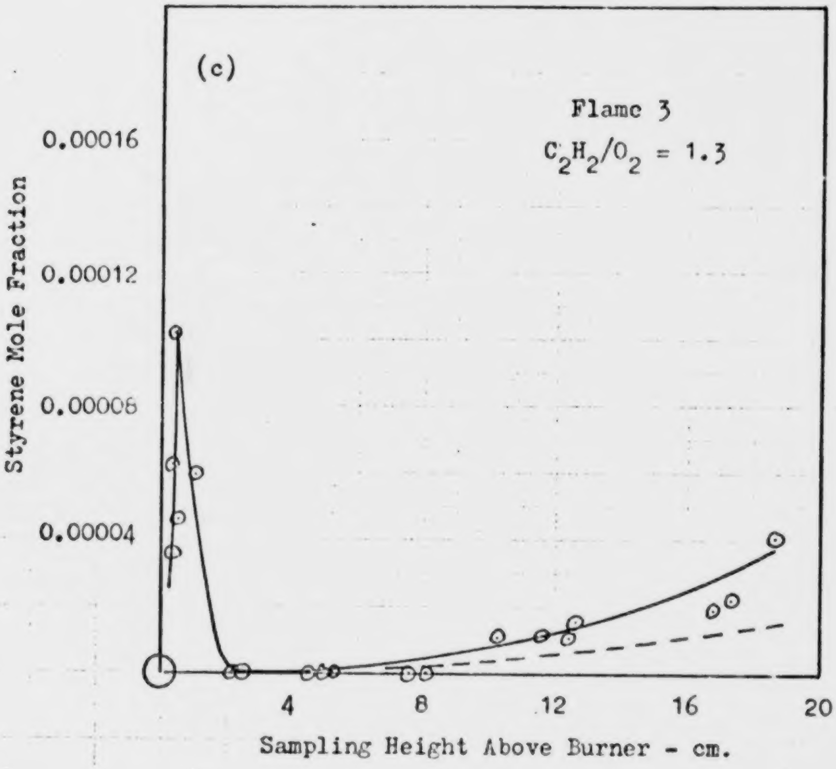


Figure 4.4.1.3.5 (c)-(d) Styrene Concentration Profiles



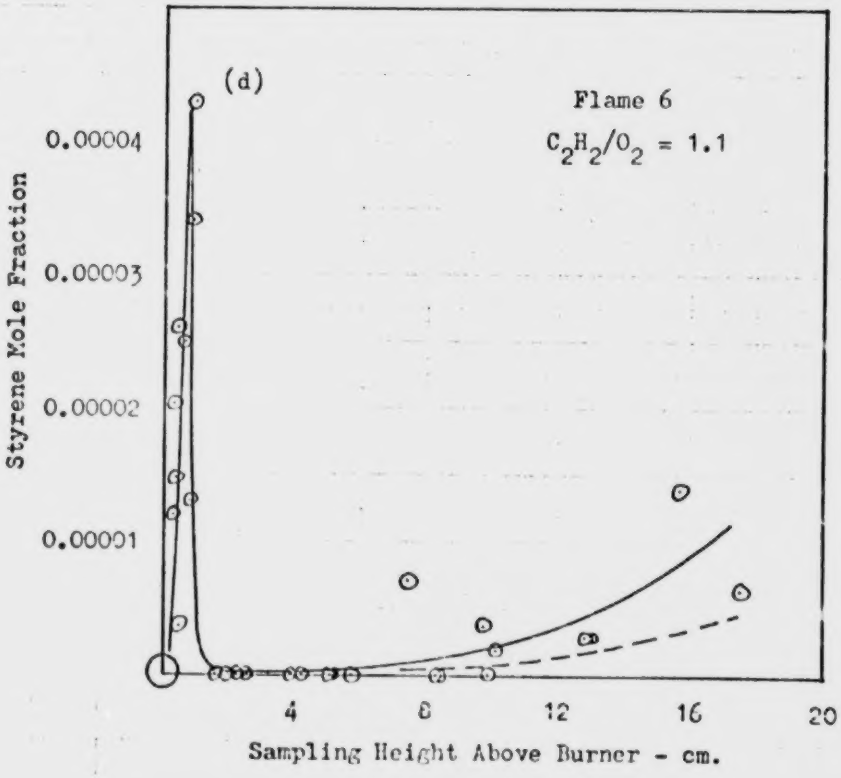


Figure 4.4.1.3.6 (a)-(b) Methyl Styrenes (?)
Concentration Profiles

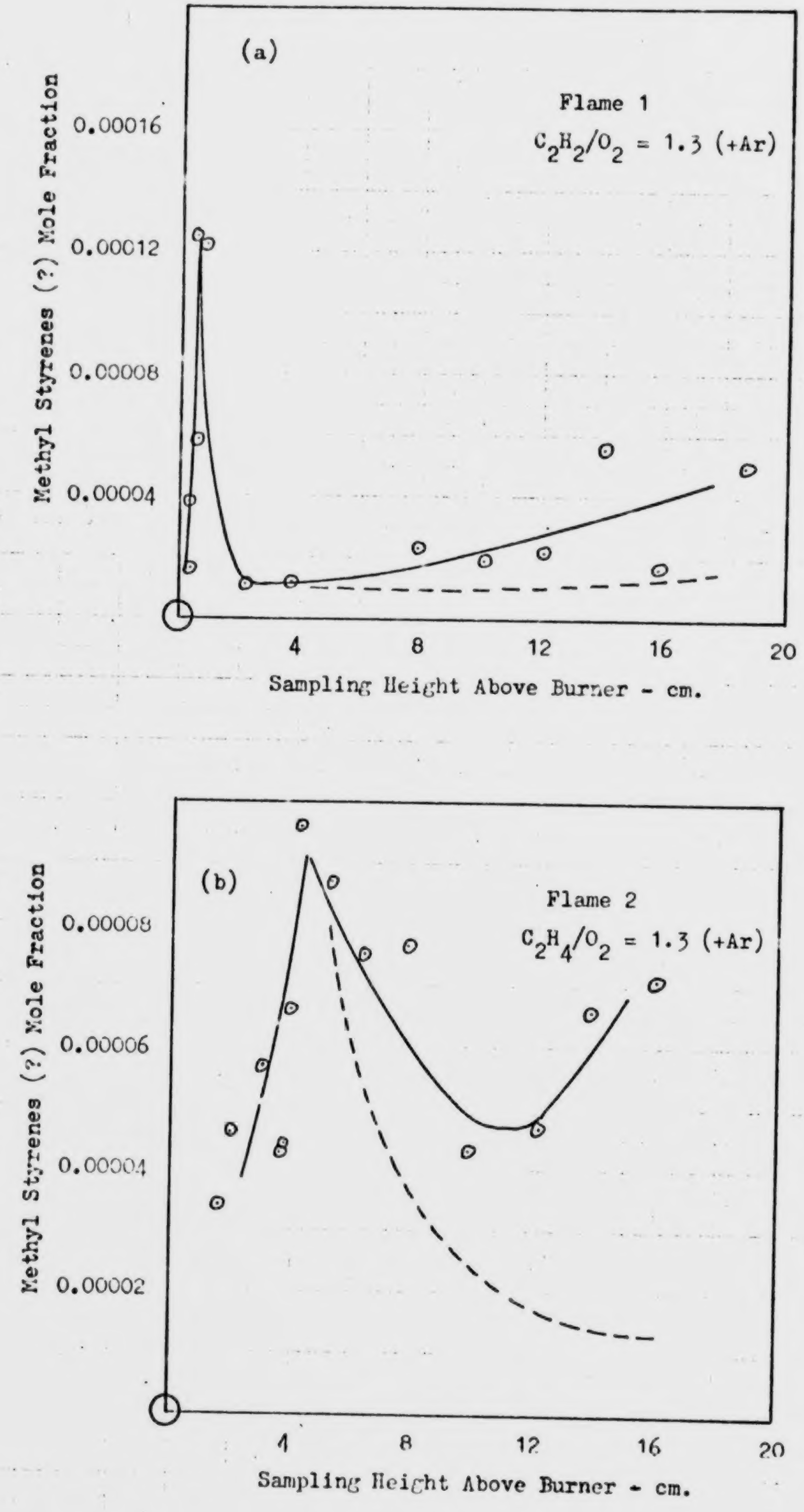


Figure 4.4.1.3.6 (c)-(d) Methyl Styrenes (?) Concentration Profiles

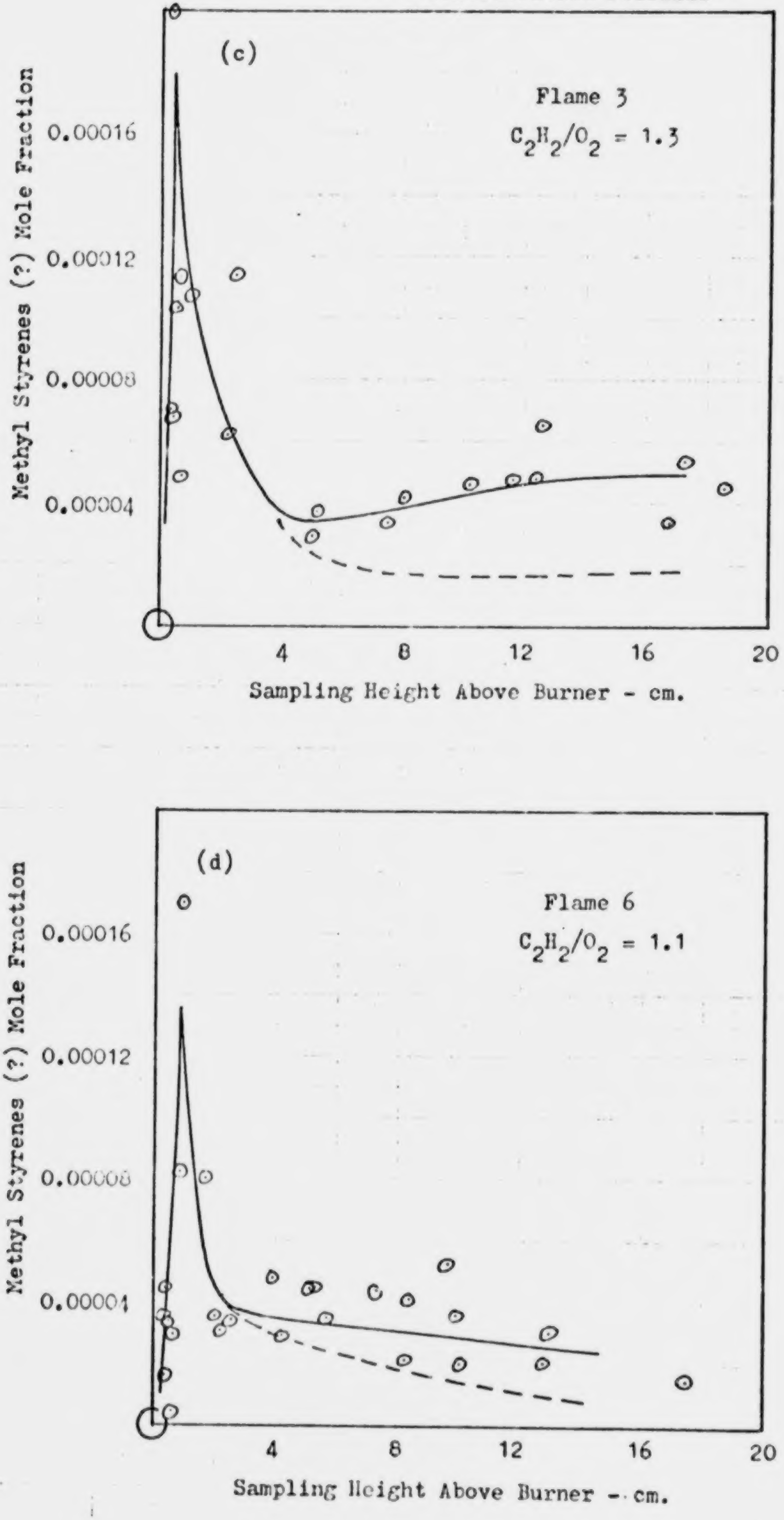


Figure 4.4.1.3.7 (a)-(b) Trimethylbenzenes (?) Concentration Profiles

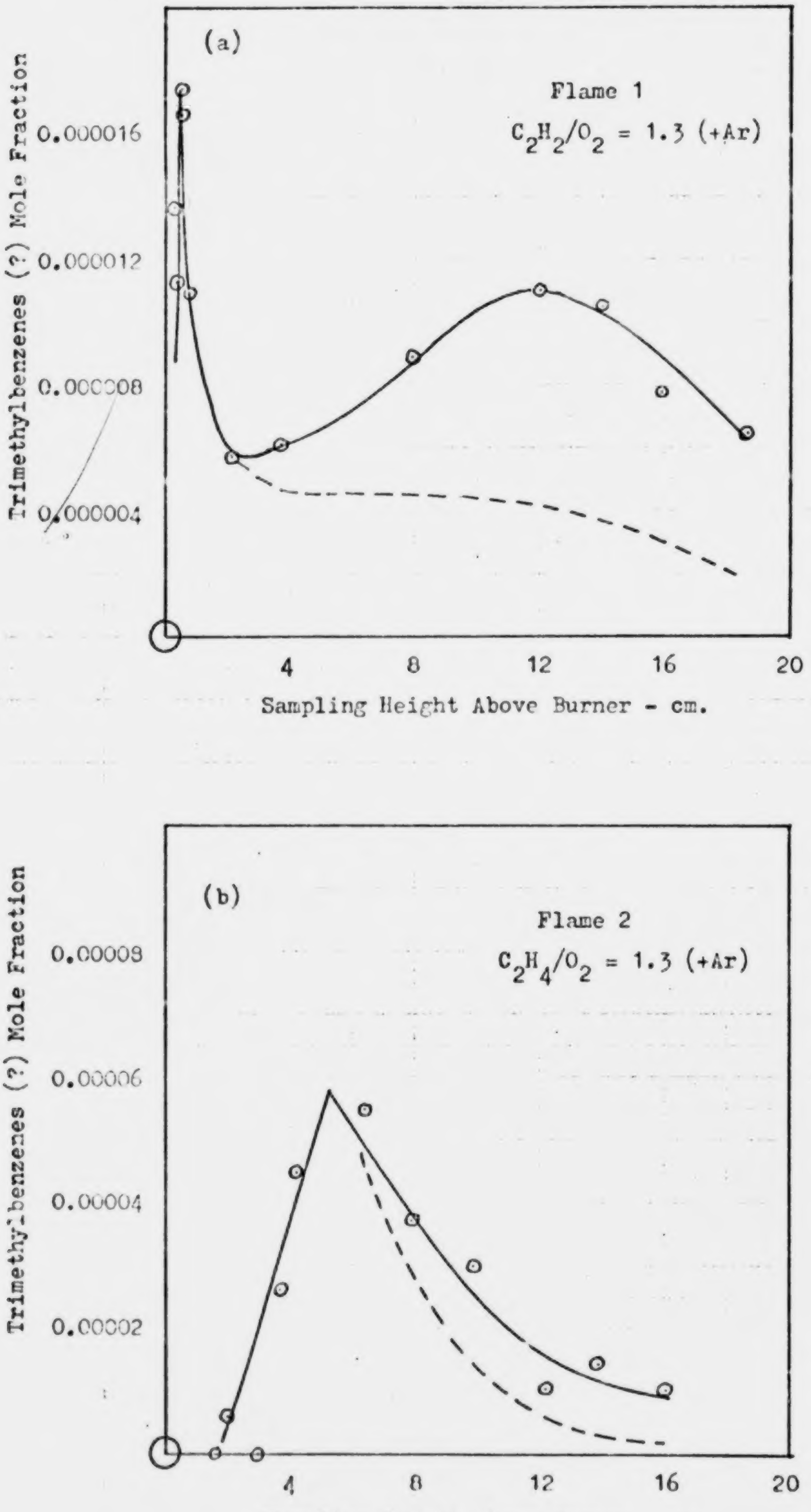


Figure 4.4.1.3.7 (c)-(d) Trimethylbenzenes (?)
Concentration Profiles

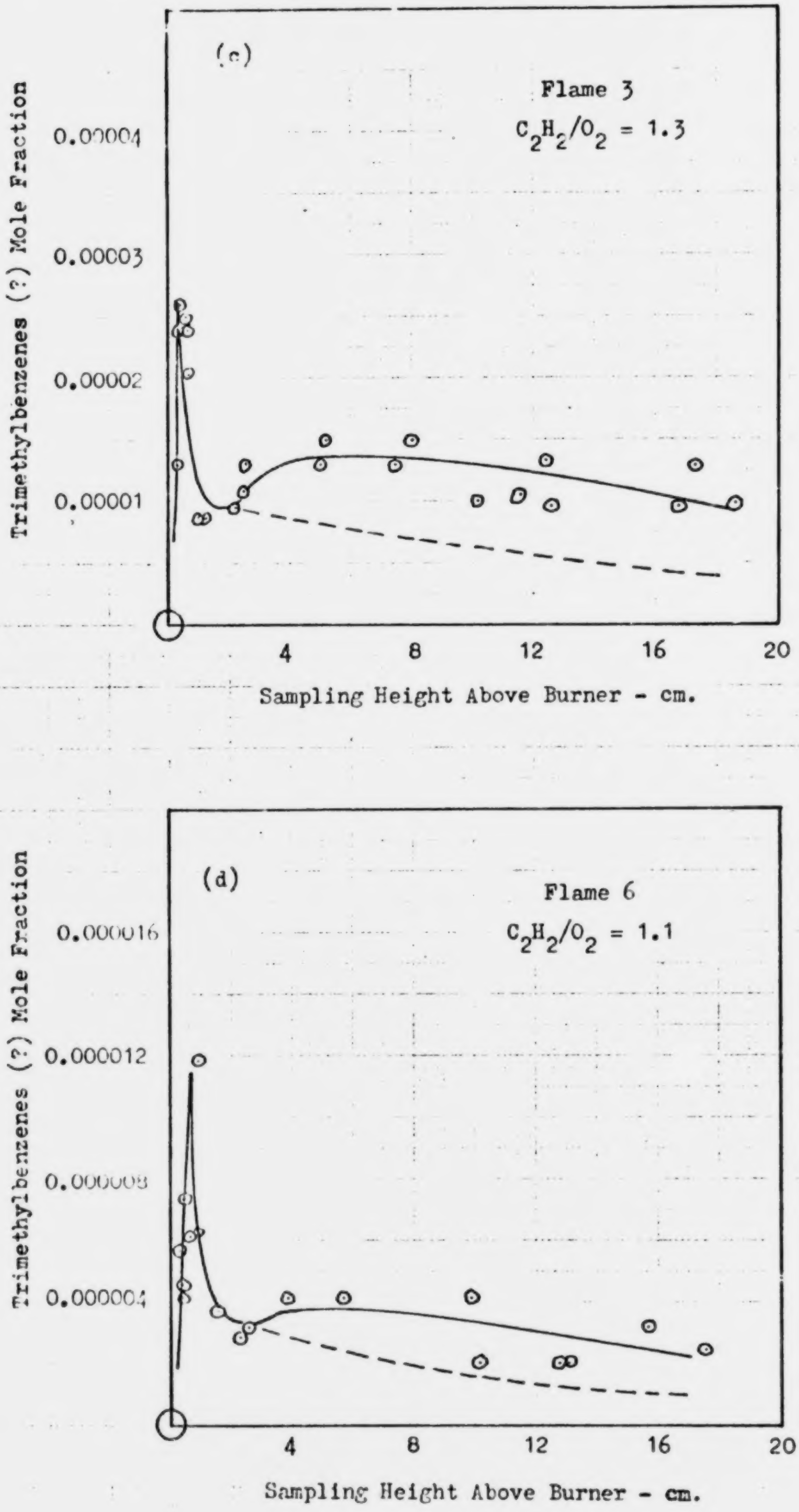


Figure 4.4.1.3.8 Indene Concentration Profiles (a)-(b)

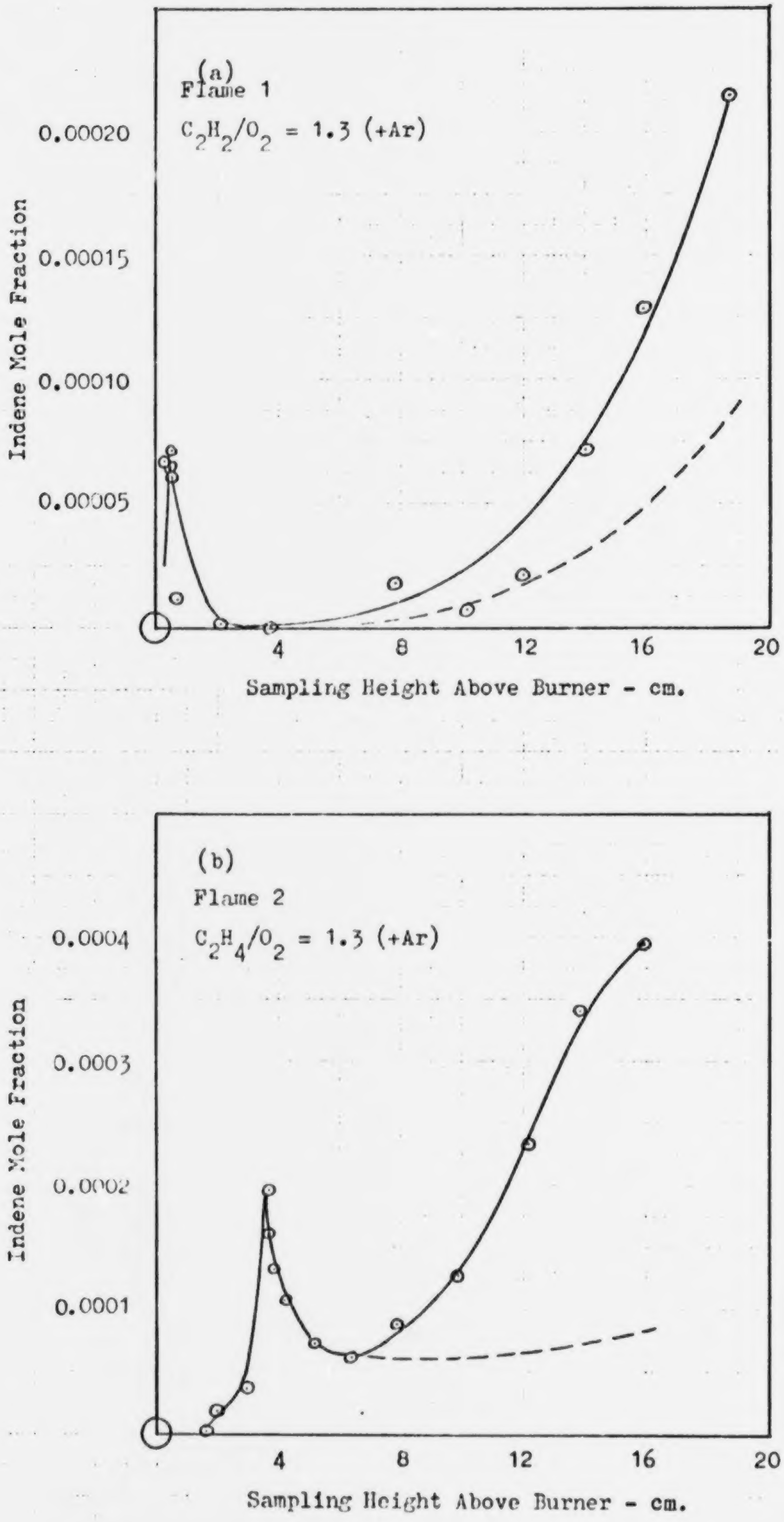
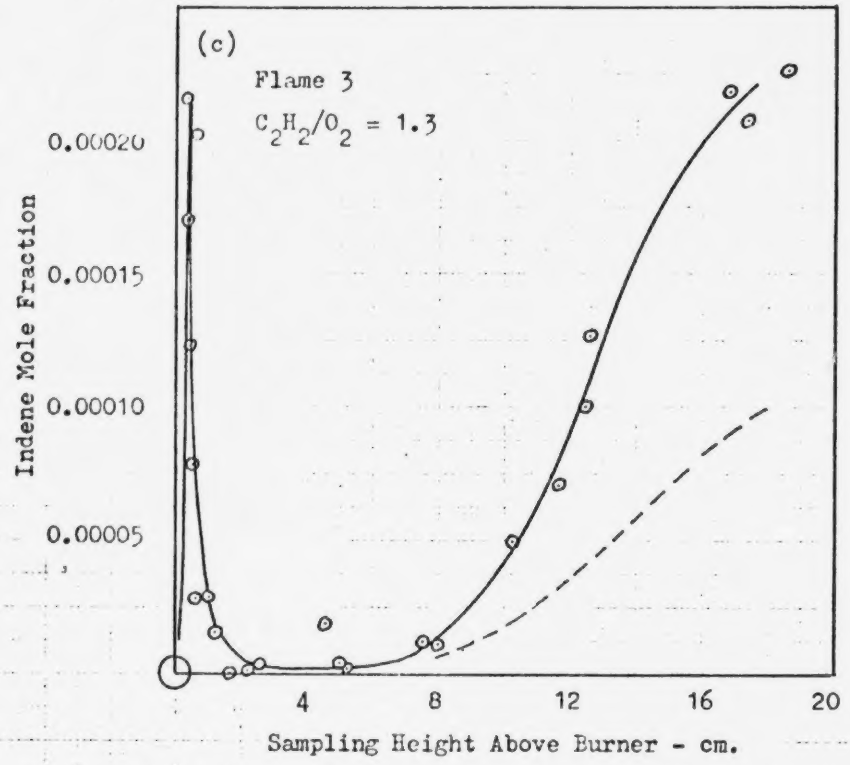


Figure 4.4.1.3.8 (c)-(d) Indene Concentration Profiles



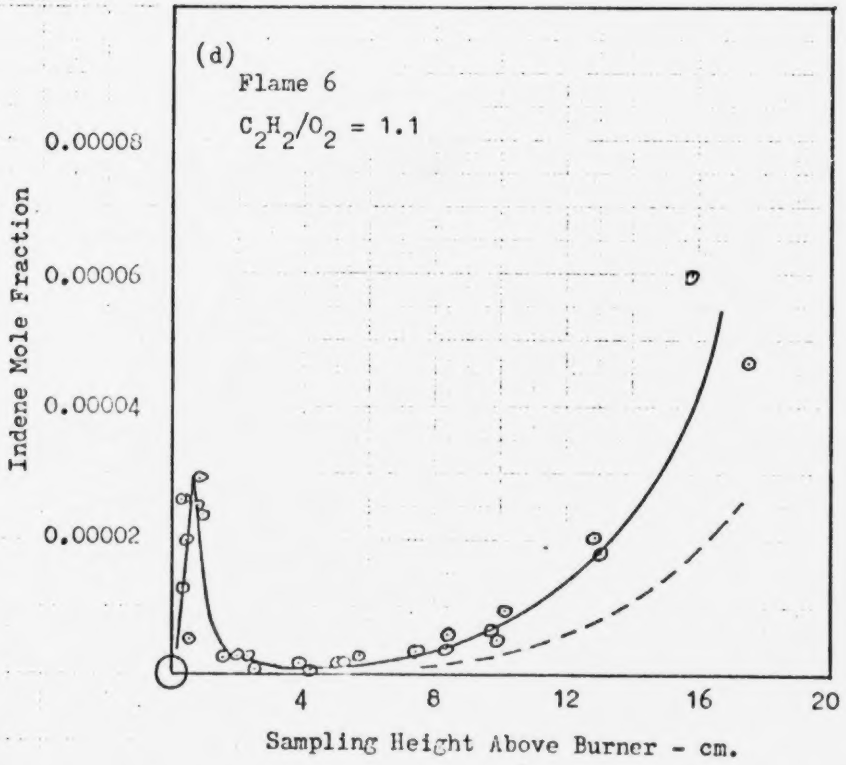
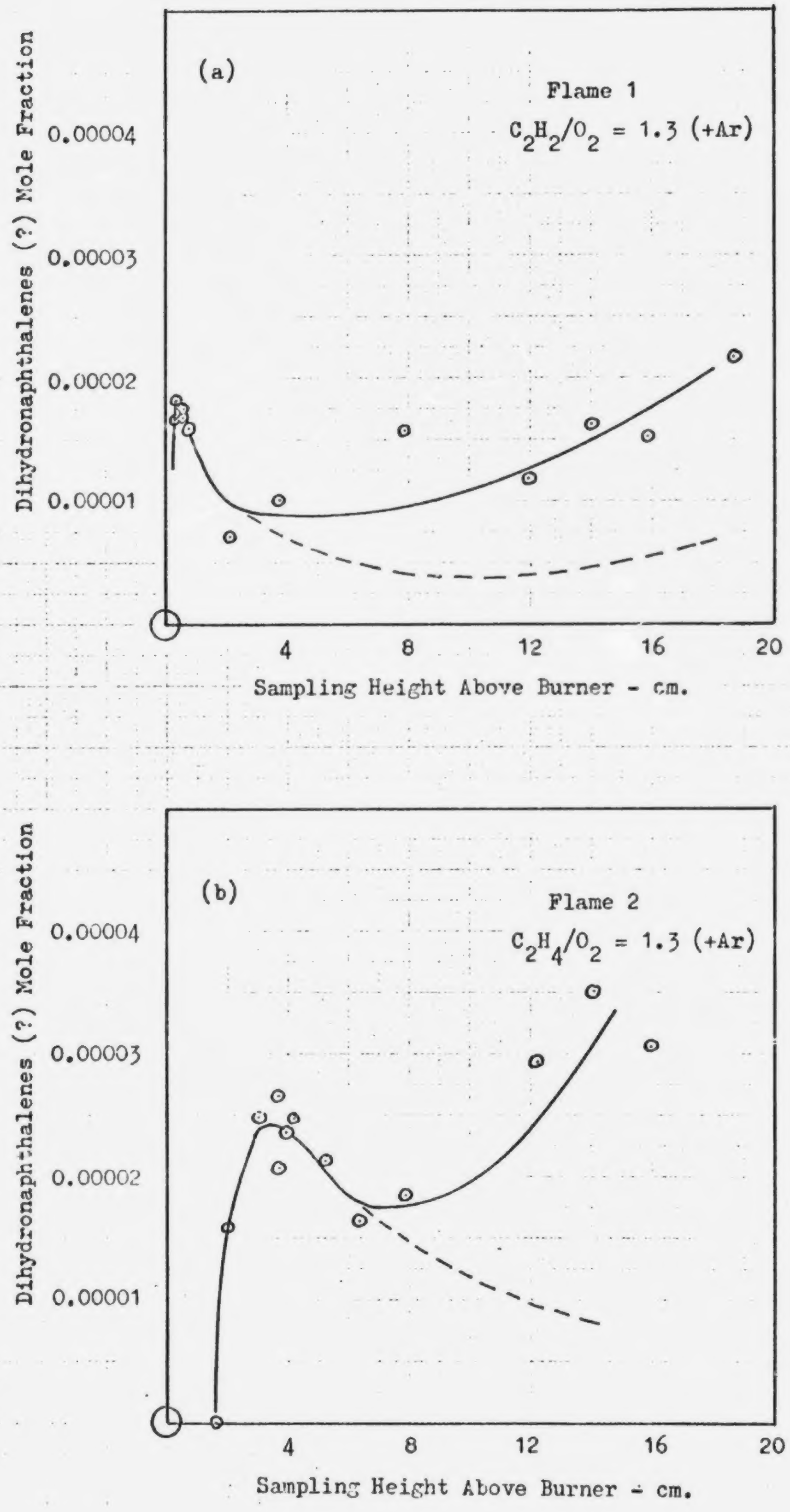


Figure 4.4.1.3.9 (a)-(b) Dihydronaphthalenes (?) Concentration Profiles



Fogure 4.4.1.3.9 (c)-(d) Dihydronaphthalenes(?)
Concentration Profiles

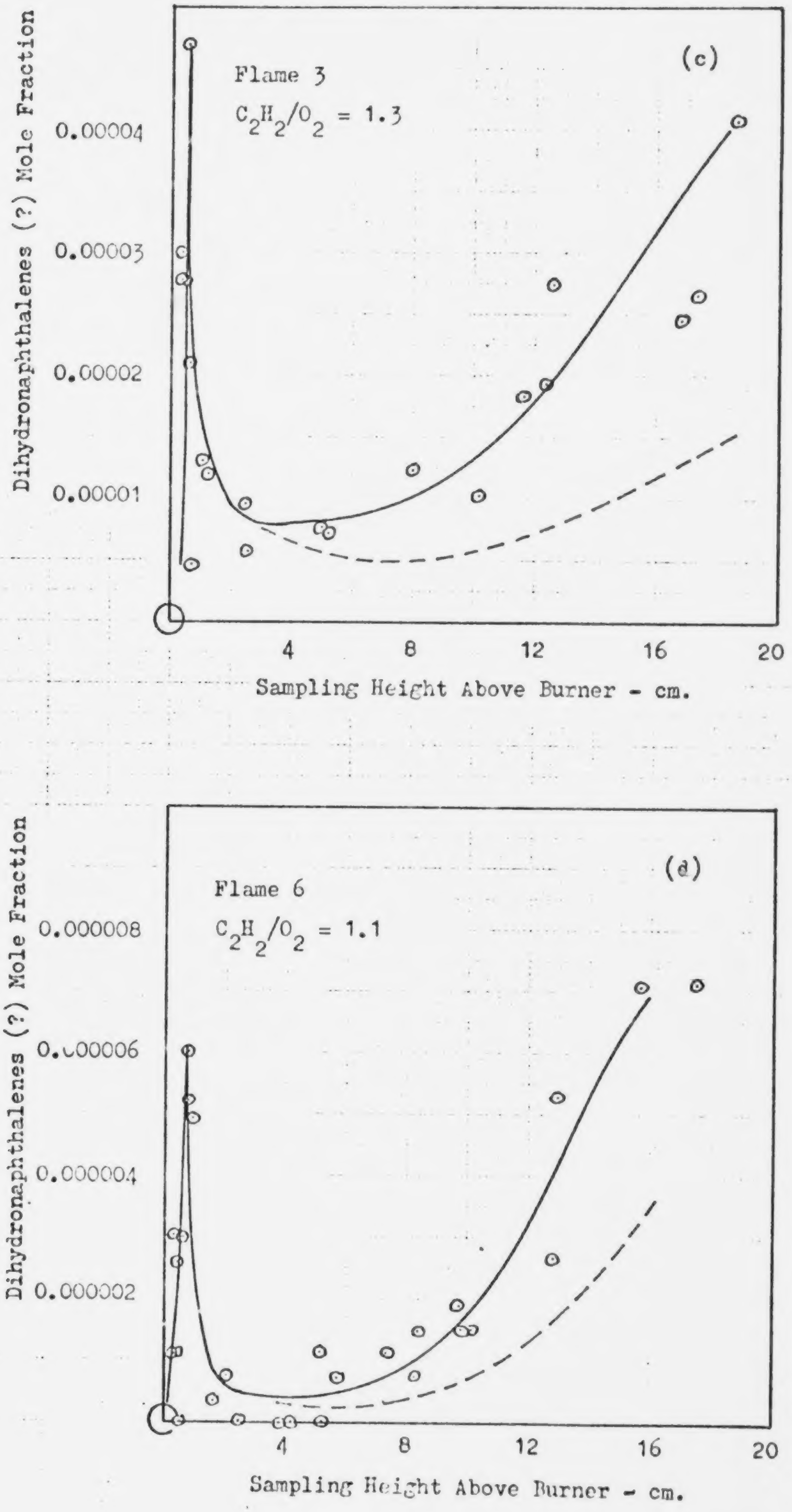


Figure 4.4.1.3.10 (a)-(b) Naphthalene Concentration Profiles

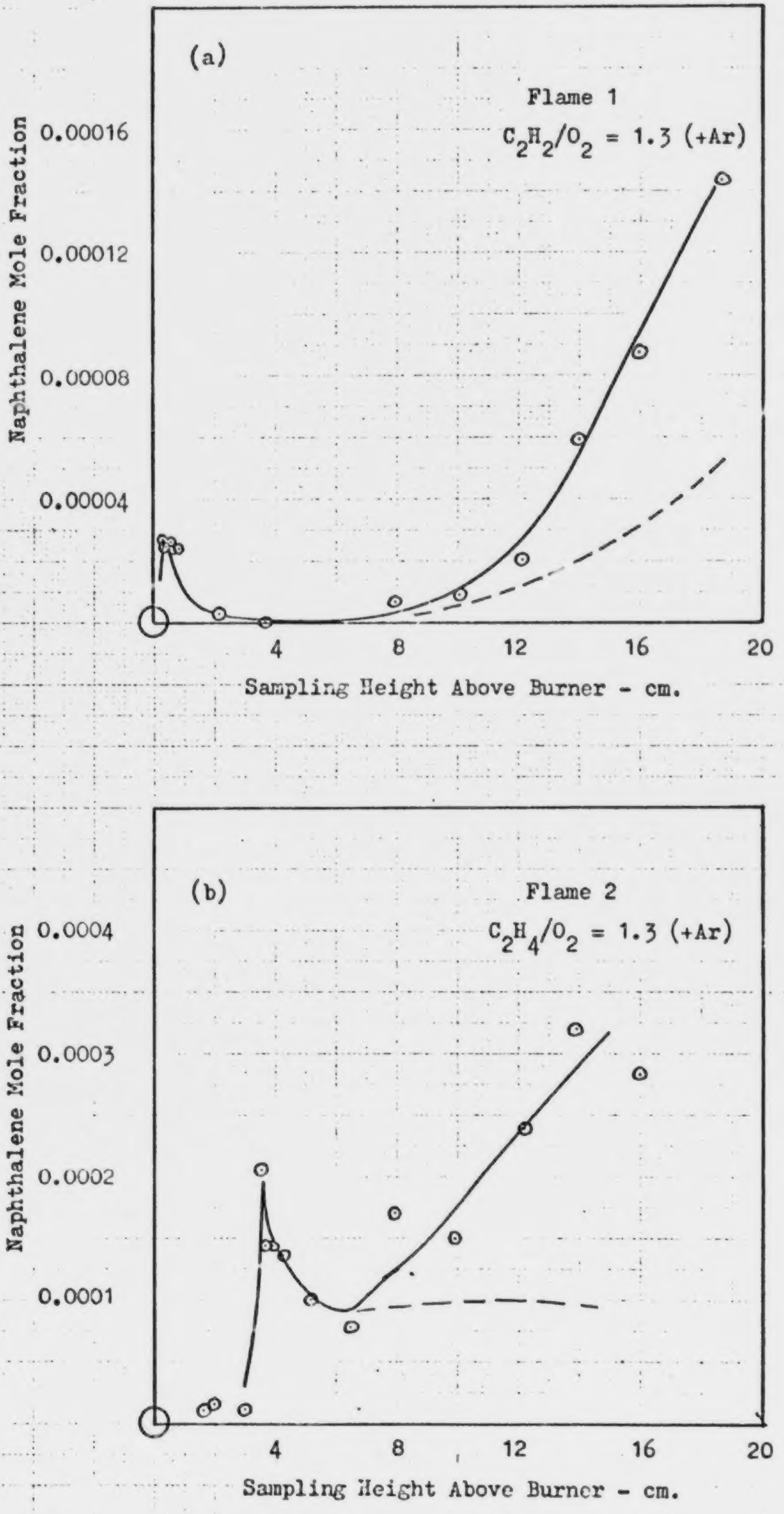


Figure 4.4.1.3.10 (c)-(d) Naphthalene Concentration Profiles

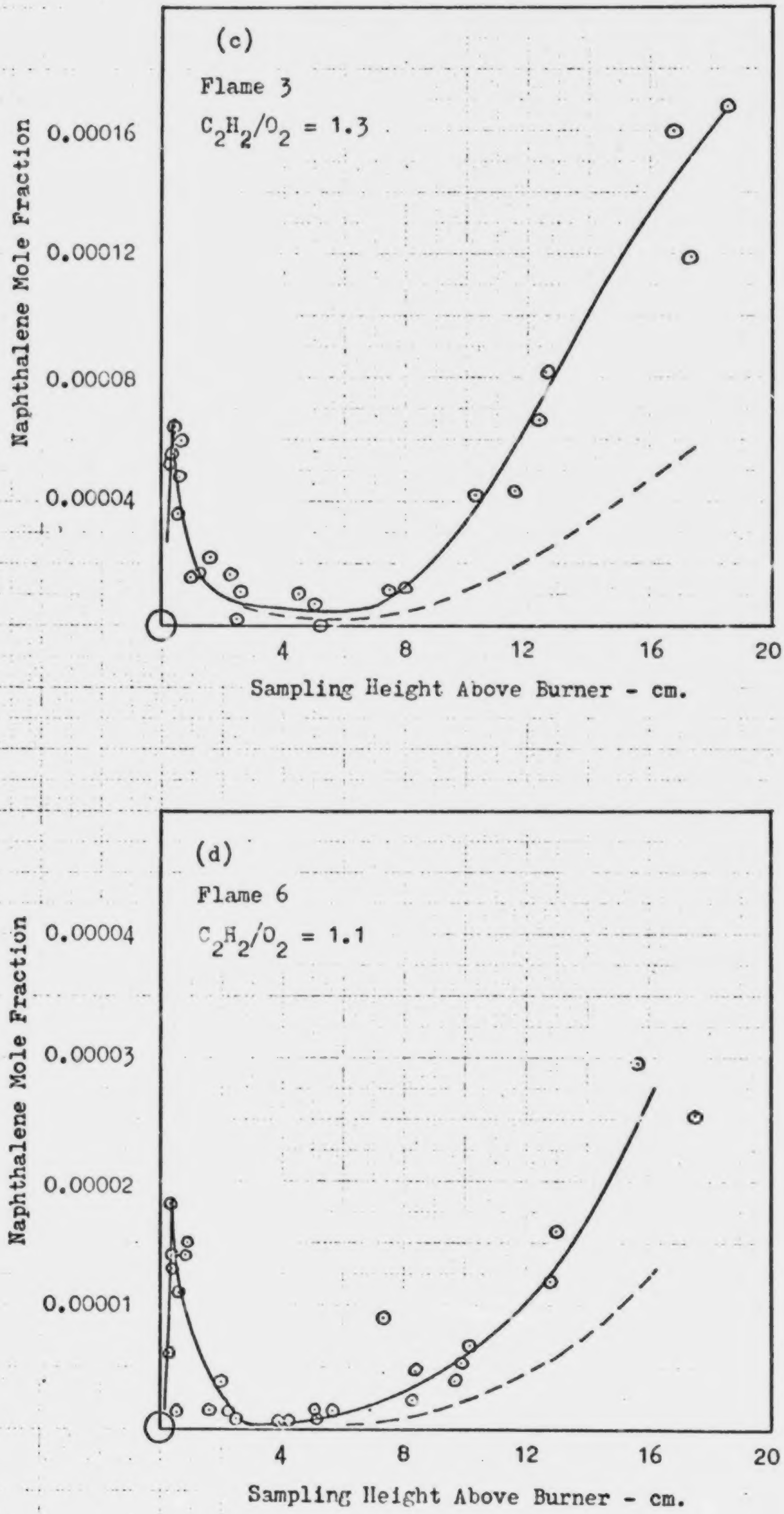
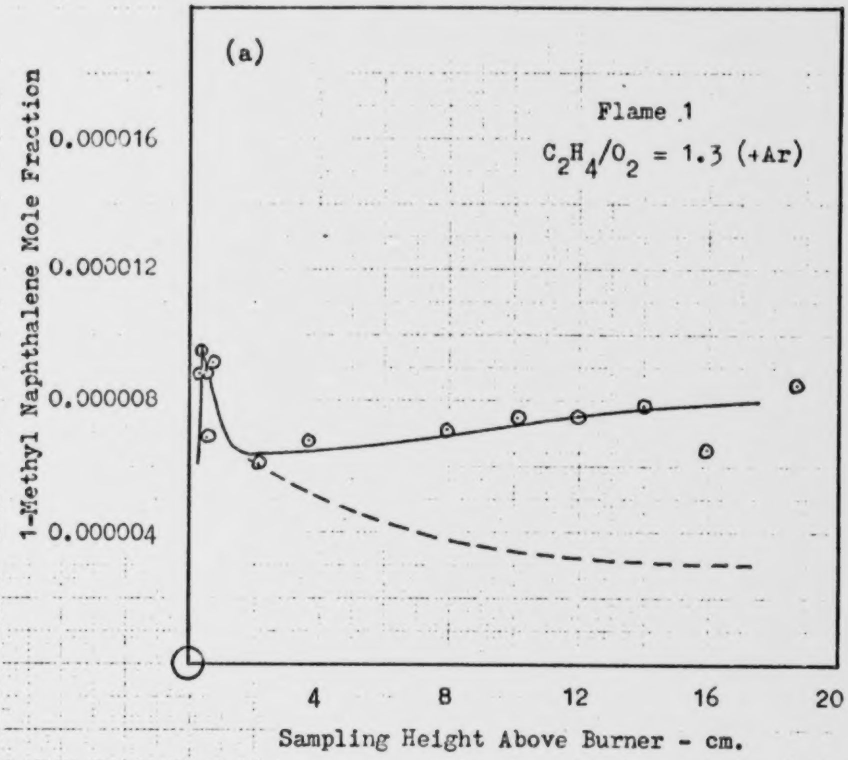


Figure 4.4.1.3.11 (a)-(b) 1-Methyl Naphthalene Concentration Profiles



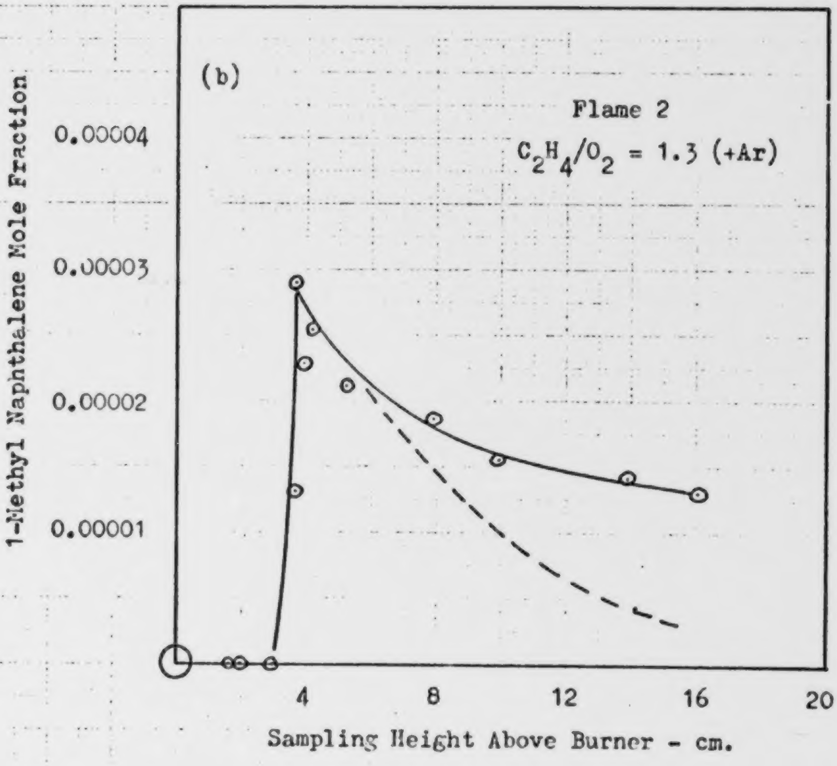


Figure 4.4.1.3.11 (c)-(d) 1-Methyl Naphthalene Concentration Profiles

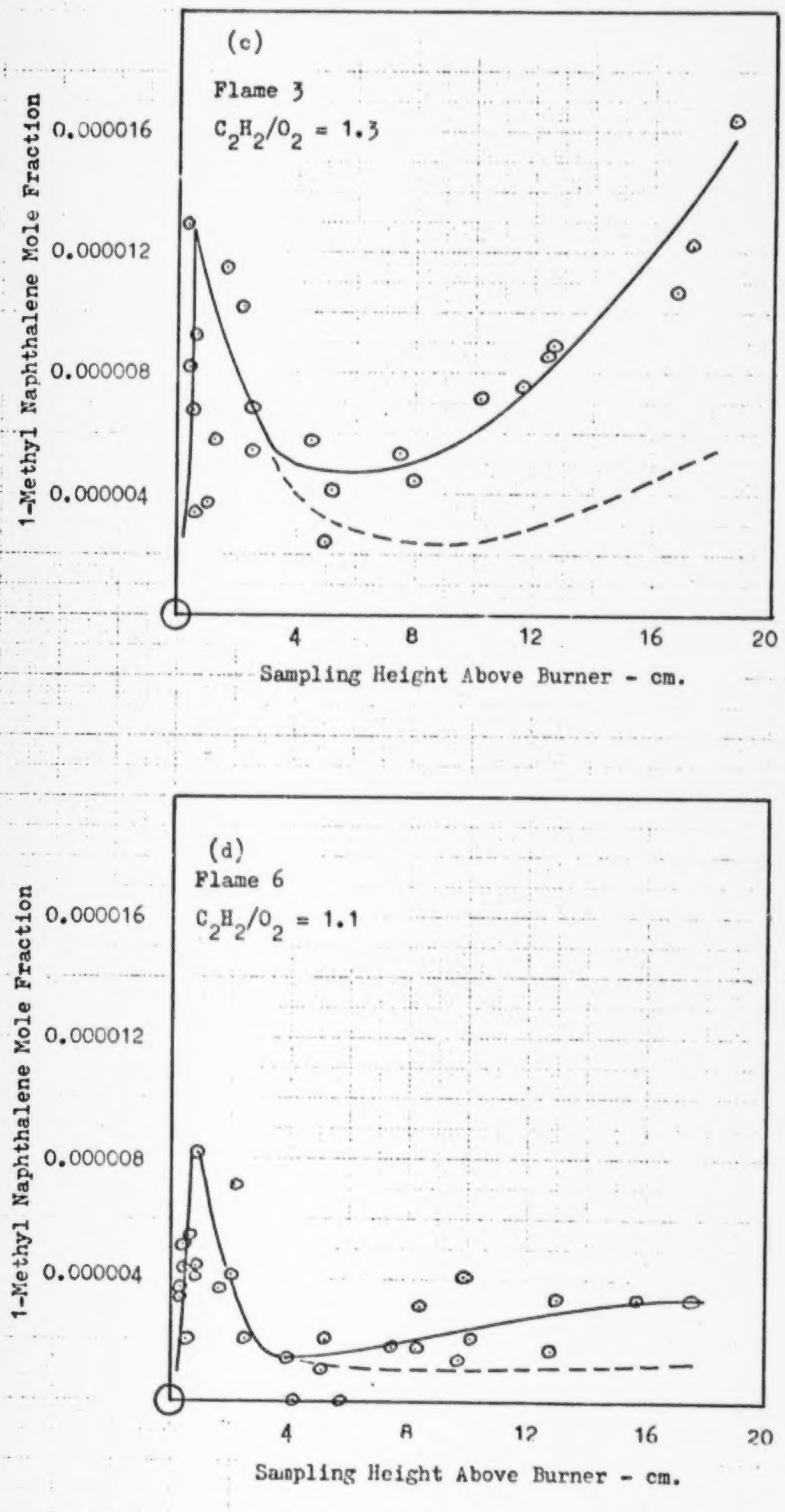


Figure 4.4.1.3.12 (a)-(b) Biphenyl Concentration Profiles

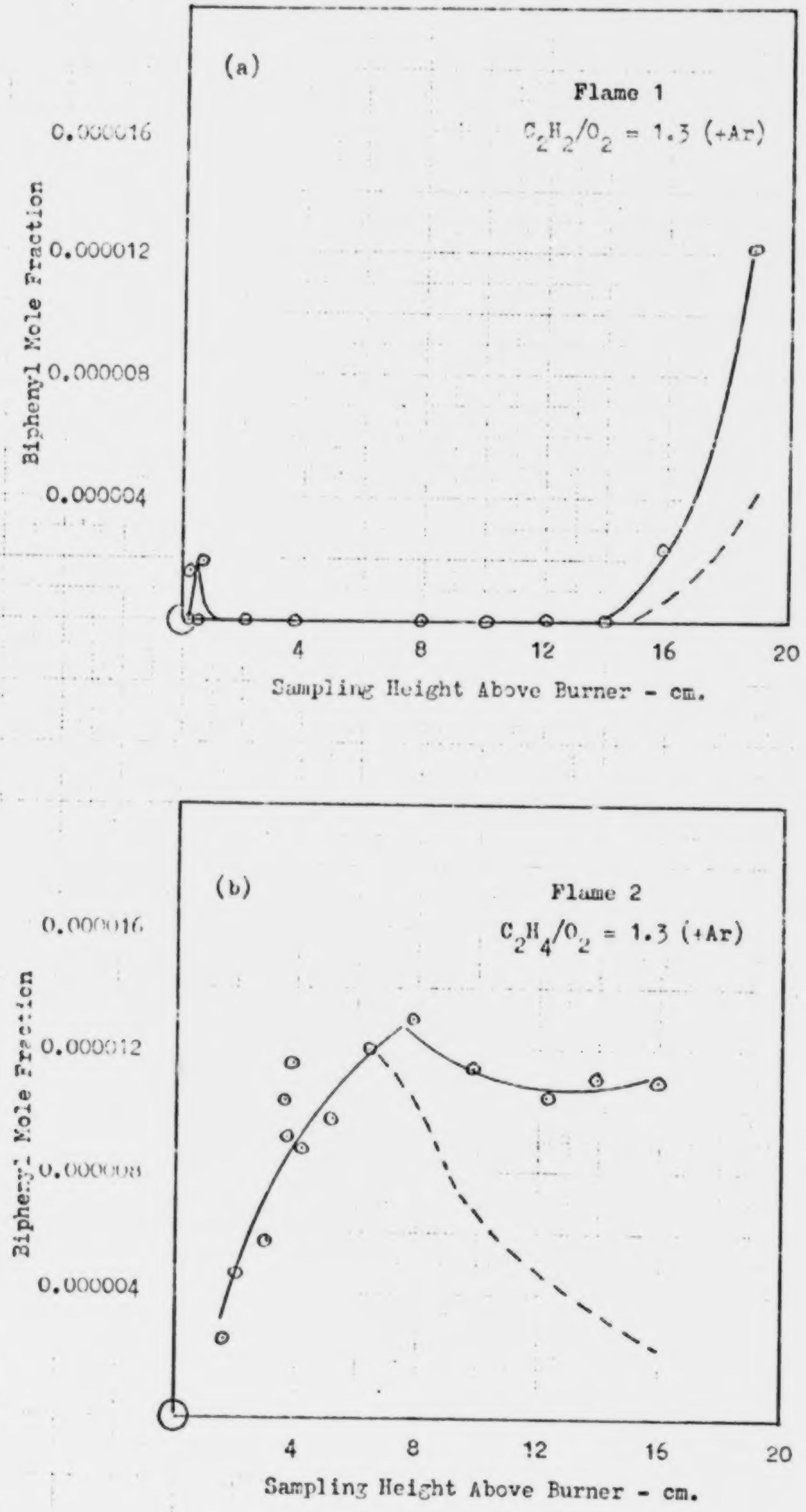


Figure 4.4.1.3.12 (c)-(d) Biphenyl Concentration Profiles

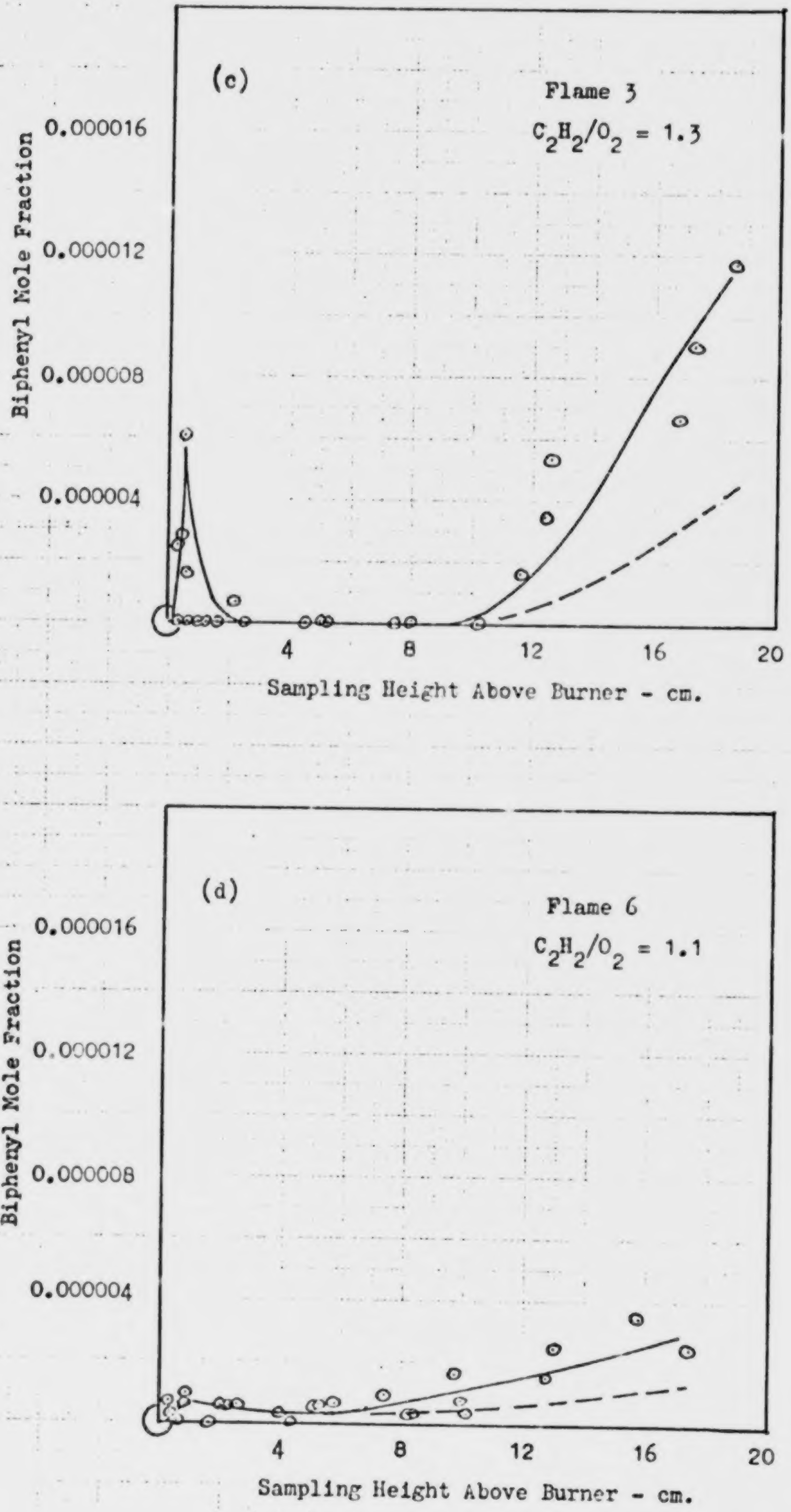


Figure 4.4.1.3.13 (a)-(b) Acenaphthylene Concentration Profiles

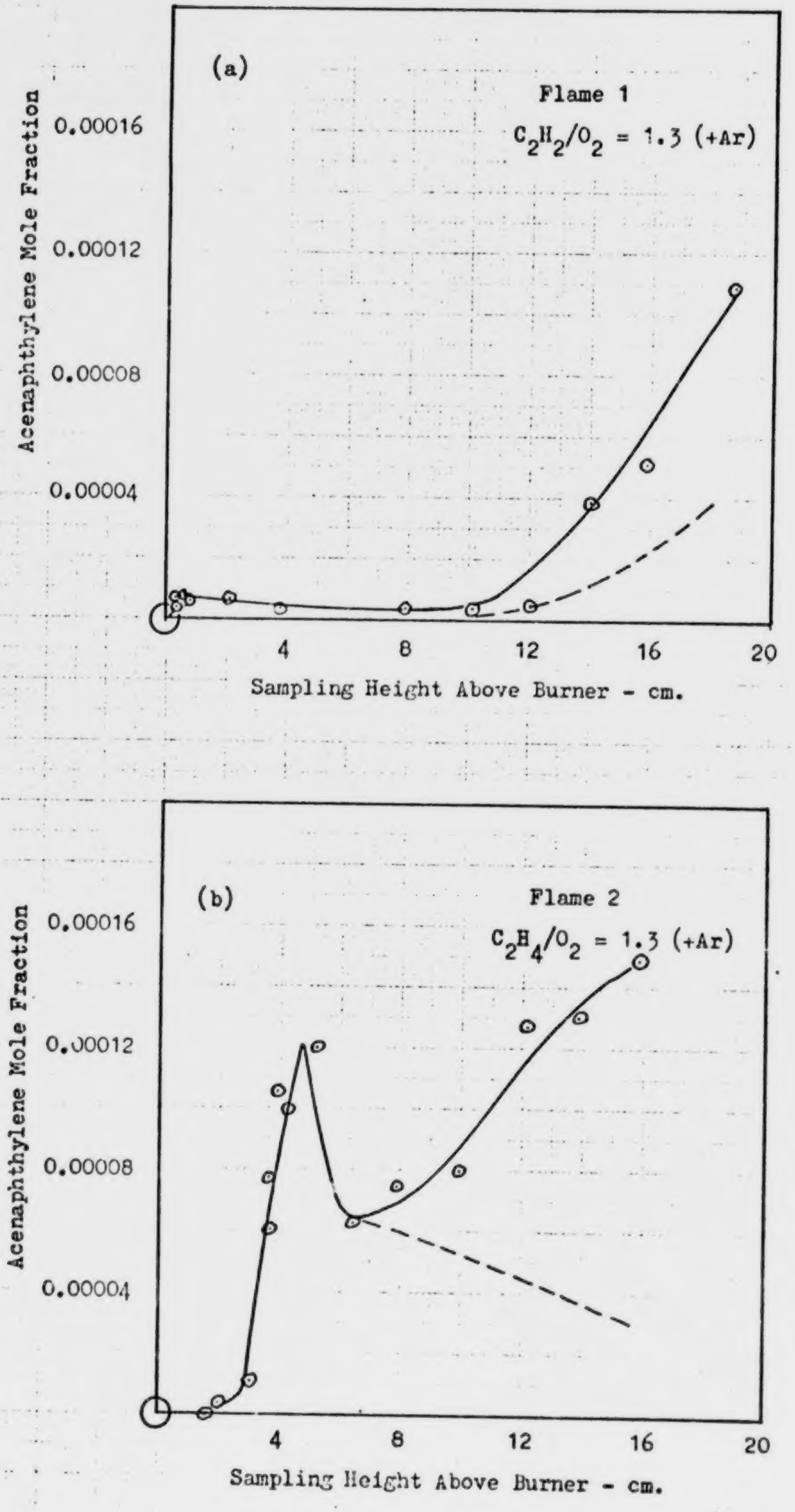


Figure 4.4.1.3.13 (c)-(d) Acenaphthylene Concentration Profiles

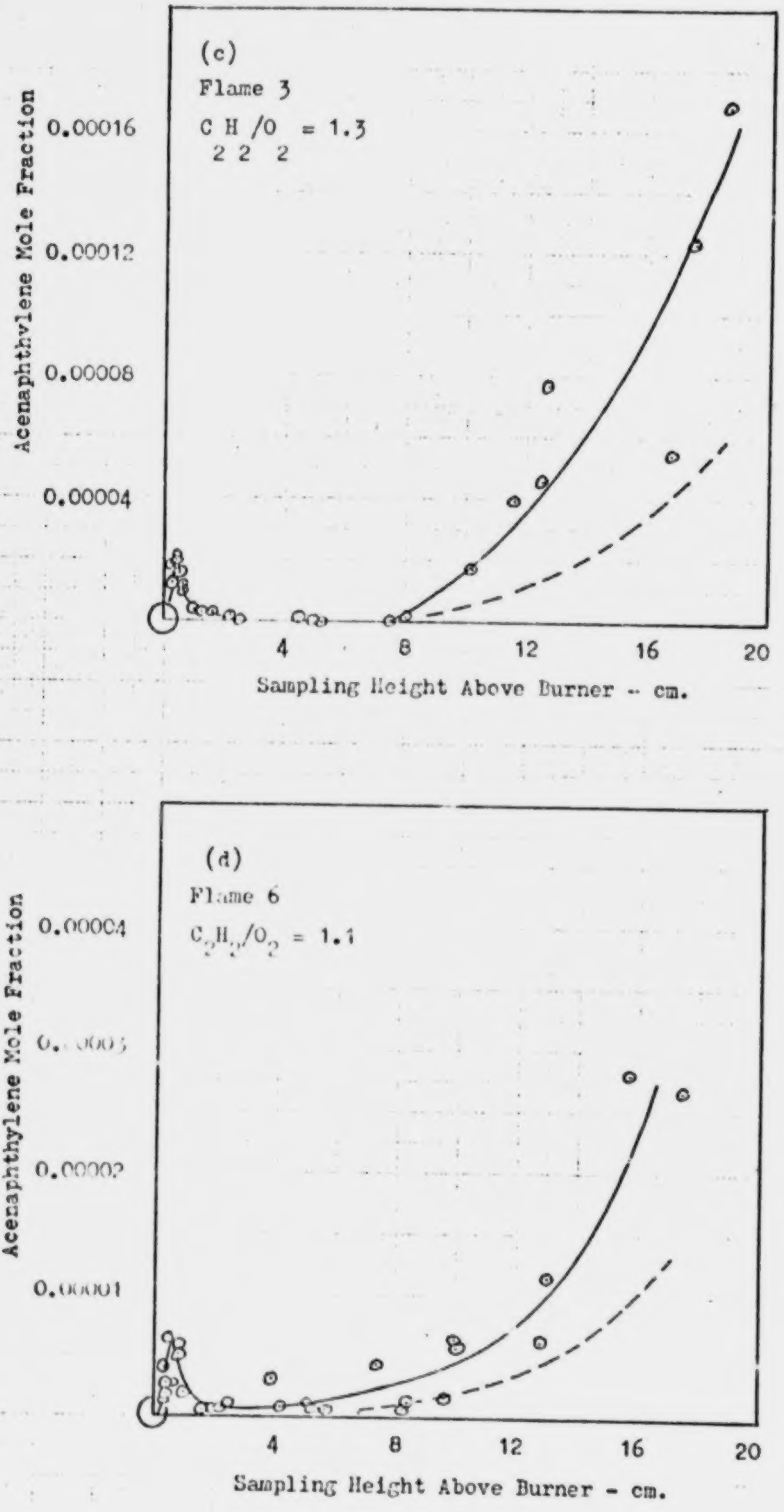
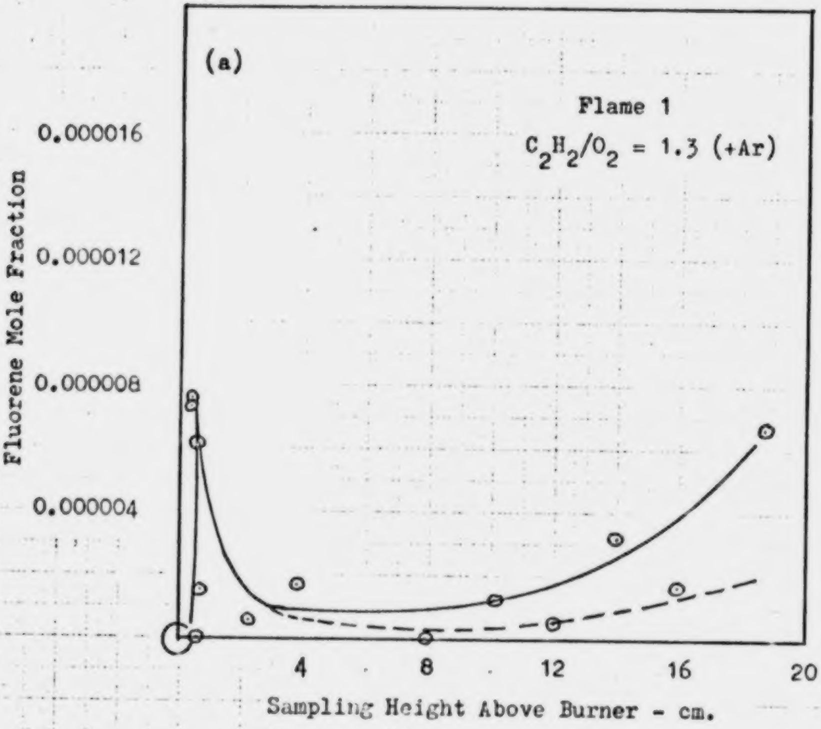


Figure 4.4.1.3.14 (a)-(b) Fluorene Concentration Profiles



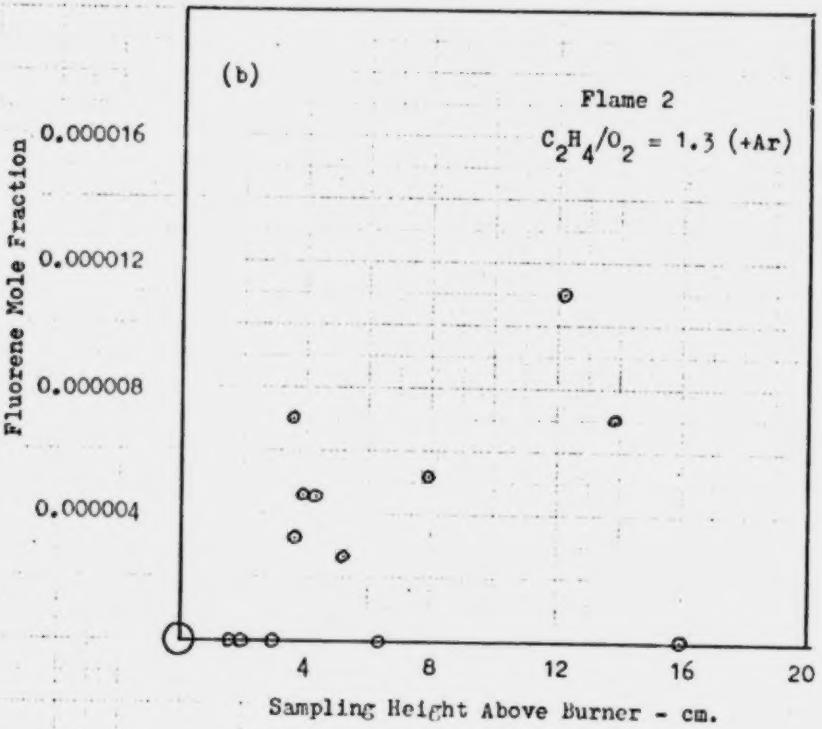
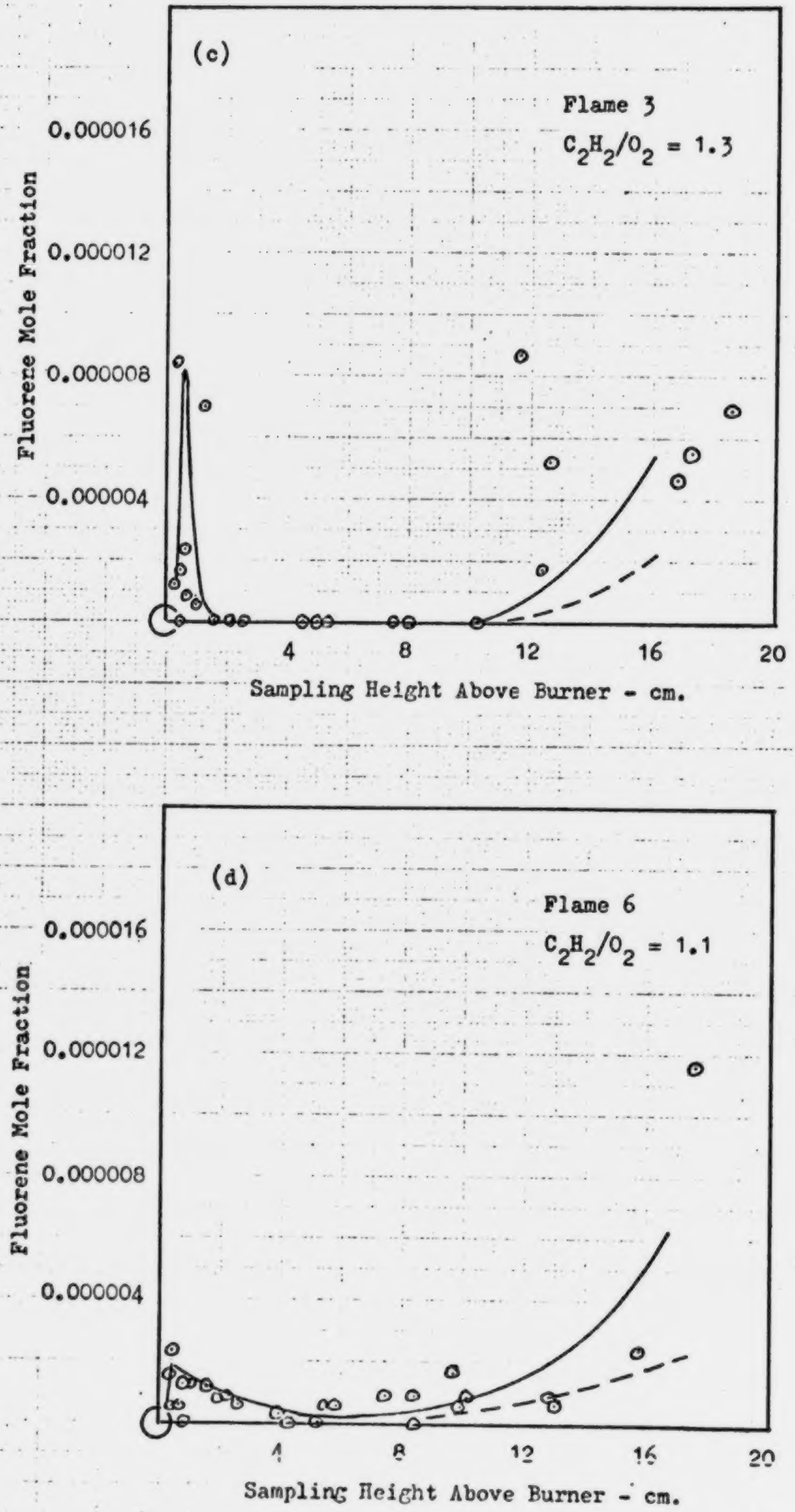


Figure 4.4.1.3.14 (c)-(d) Fluorene Concentration Profiles



Although other higher molecular weight pcah (e.g. the benzopyrenes) have been found in soot, insufficient quantities of these compounds are sampled in this study to allow detection by gas chromatography.

4.4.2.3 Concentration Profiles of Extraction Filter Products

The concentration profiles of the larger peaks in the extraction filter products are presented in Figures 4.4.2.3.1 to 4.4.2.3.12. Since G.L.C. Peaks 30, 34, 35, 36 and 37 are often too small to be measured with any reasonable degree of accuracy, the concentration profiles of the species which produce these peaks are, therefore, not presented.

The concentration profiles of the following peaks are presented:

Indene	in Figures 4.4.2.3.1(a)-(c)
Naphthalene	in Figures 4.4.2.3.2(a)-(c)
1-Methyl Naphthalene	in Figures 4.4.2.3.3(a)-(c)
Acenaphthylene	in Figures 4.4.2.3.4(a)-(c)
Fluorene	in Figures 4.4.2.3.5(a)-(c)
1.8,4.5-bi(etheno-)naphthalene(?) (m/e = 176)	in Figures 4.4.2.3.6(a)-(c)
Anthracene + Phenanthrene	in Figures 4.4.2.3.7(a)-(c)
4.5-methylene phenanthrene	in Figures 4.4.2.3.8(a)-(c)
Fluoranthene	in Figures 4.4.2.3.9(a)-(c)
Pyrene	in Figures 4.4.2.3.10(a)-(c)
Benzofluorenes	in Figures 4.4.2.3.11(a)-(c)
Methyl Pyrenes	in Figures 4.4.2.3.12(a)-(c)

There is considerable scatter in the experimental results for the methyl pyrenes concentration profiles, this probably being due to the errors involved in measuring such low concentrations.

The concentration profiles of all species are very similar for Flames 1 and 3 (the oxy-acetylene flames). For indene, naphthalene, 1-methyl naphthalene, fluorene, 1.8,4.5-bi-(etheno-)naphthalene (?), fluoranthene and pyrene the results show that the addition of argon makes little difference to the concentration although for species such as acenaphthylene, anthracene + phenanthrene and the benzofluorene fraction, the addition of argon tends to increase the concentration. One might expect, as in the case of 4.5-methylene phenanthrene, that the addition of argon to a flame would tend to reduce concentrations.

For the lower molecular weight species collected in the extraction filter (i.e., indene, naphthalene, 1-methyl naphthalene, acenaphthylene and anthracene + phenanthrene) the concentrations of species in the yellow zone of Flames 1 and 3 (the acetylene flames) remain roughly constant although for the higher molecular weight species (i.e., 1.8,4.5-bi-(etheno-) naphthalene, 4.5-methylene phenanthrene, fluoranthene, pyrene and the benzofluorene fraction), there is some increase in concentration. There is a slight increase in the concentration of fluorene in the yellow zones of Flames 1 and 3. This increase in concentration may be attributed to the pyrolysis of lower molecular weight species in the flame although the results of this study do not indicate clearly what these species might be.

As may be seen in Figures 4.4.2.3.1 to 4.4.2.3.12 there is an initial rapid increase in concentration of all species in the blue zone of the oxy-acetylene flames and a maximum concentration is reached before the end of this zone. These species are then destroyed to a certain extent (but not completely), possibly by $\dot{O}H$ radicals or other oxygenated radicals. (N.B. this is the region in the flame where the oxygen concentration rapidly falls to zero) The initial peak in concentration is also shown in Flame 2 (the oxy-ethylene flame) for several species including indene, naphthalene, 1-methyl naphthalene, acenaphthylene, fluorene, 1.8,4.5-bi-(etheno-)naphthalene (?), 4.5-methylene phenanthrene and fluoranthene. The concentration profiles of anthracene + phenanthrene and pyrene apparently show a fairly steady rise throughout this flame, although when these profiles are corrected for the change in density of the flame gases, a maximum value is observable beyond the blue region.

Figure 4.4.2.3.1 (a)-(c) Indene Concentration Profiles

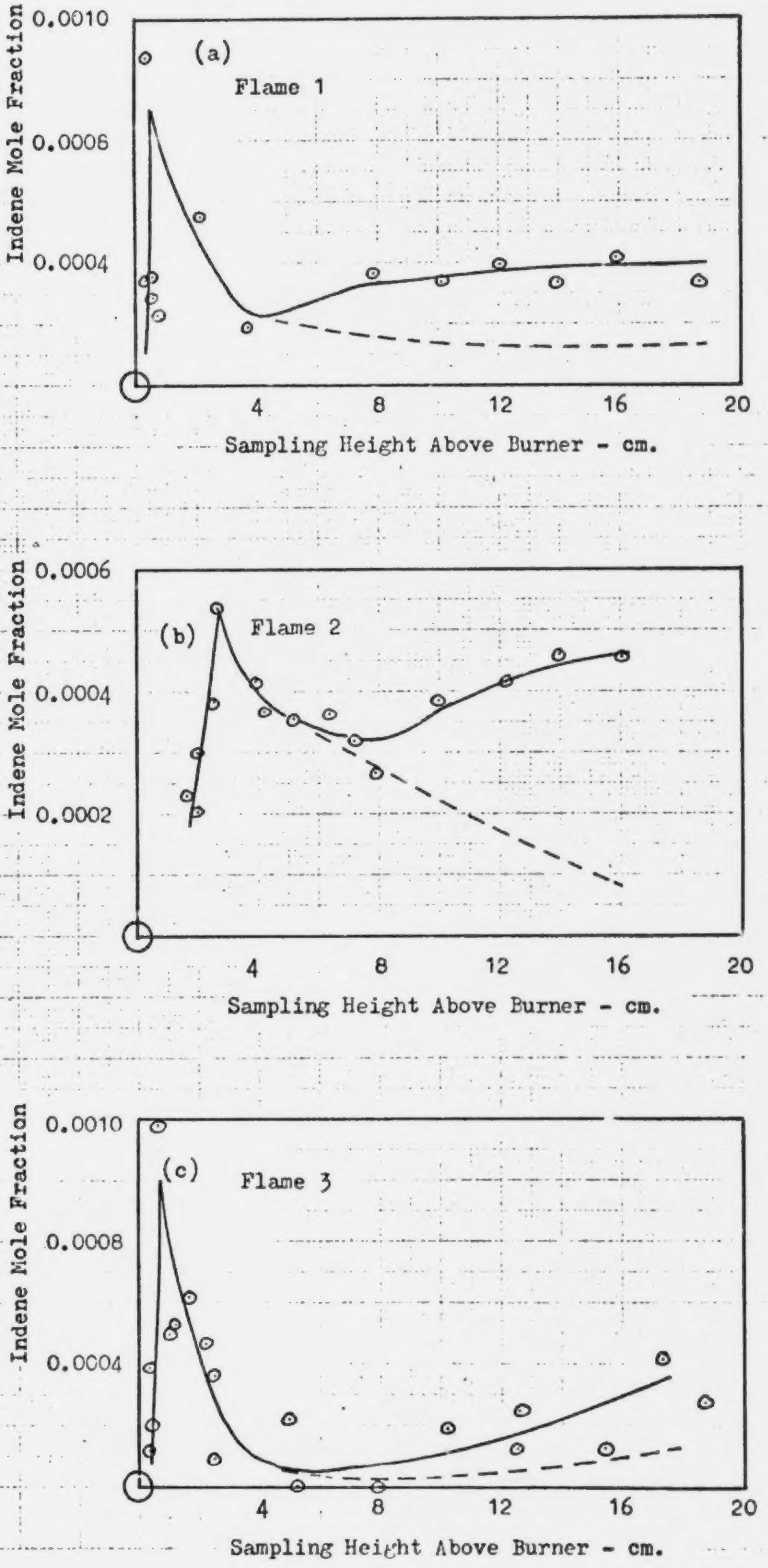


Figure 4.4.2.3.2 (a)-(c) Naphthalene Concentration Profiles

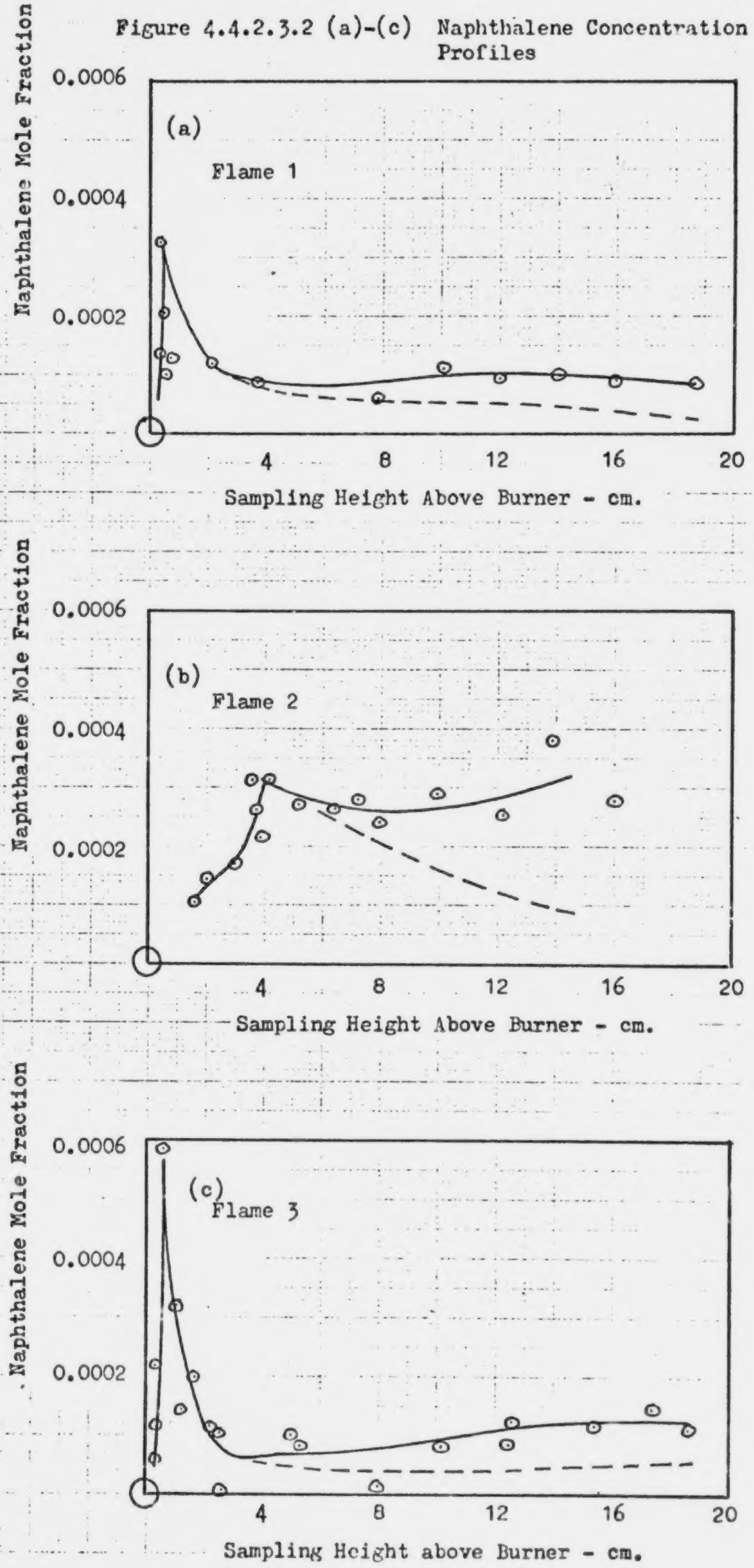


Figure 4.4.2.3.3 (a)-(c) 1-Methyl Naphthalene Concentration Profiles

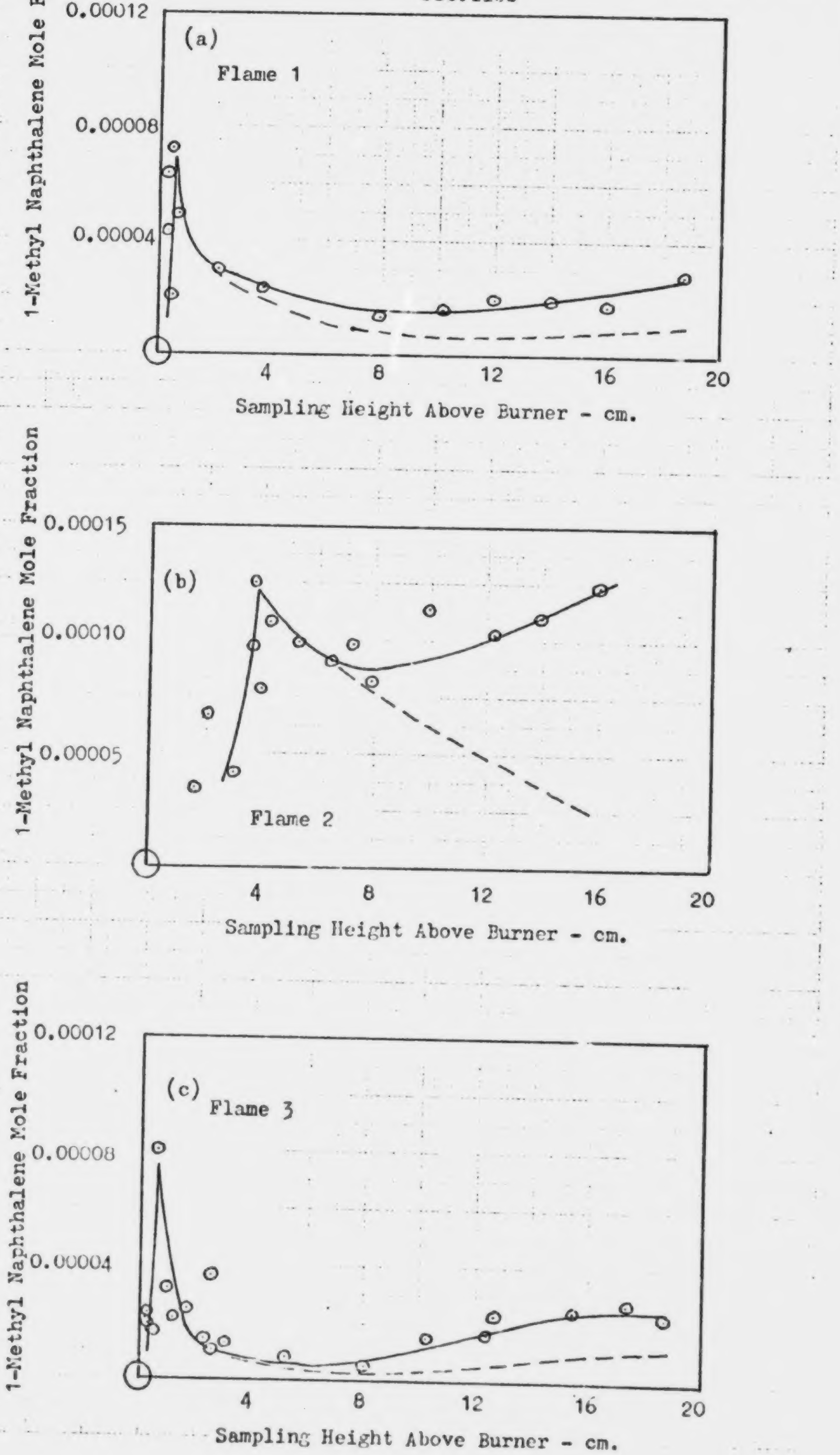


Figure 4.4.2.3.4 (a)-(c) Acenaphthylene Concentration Profiles

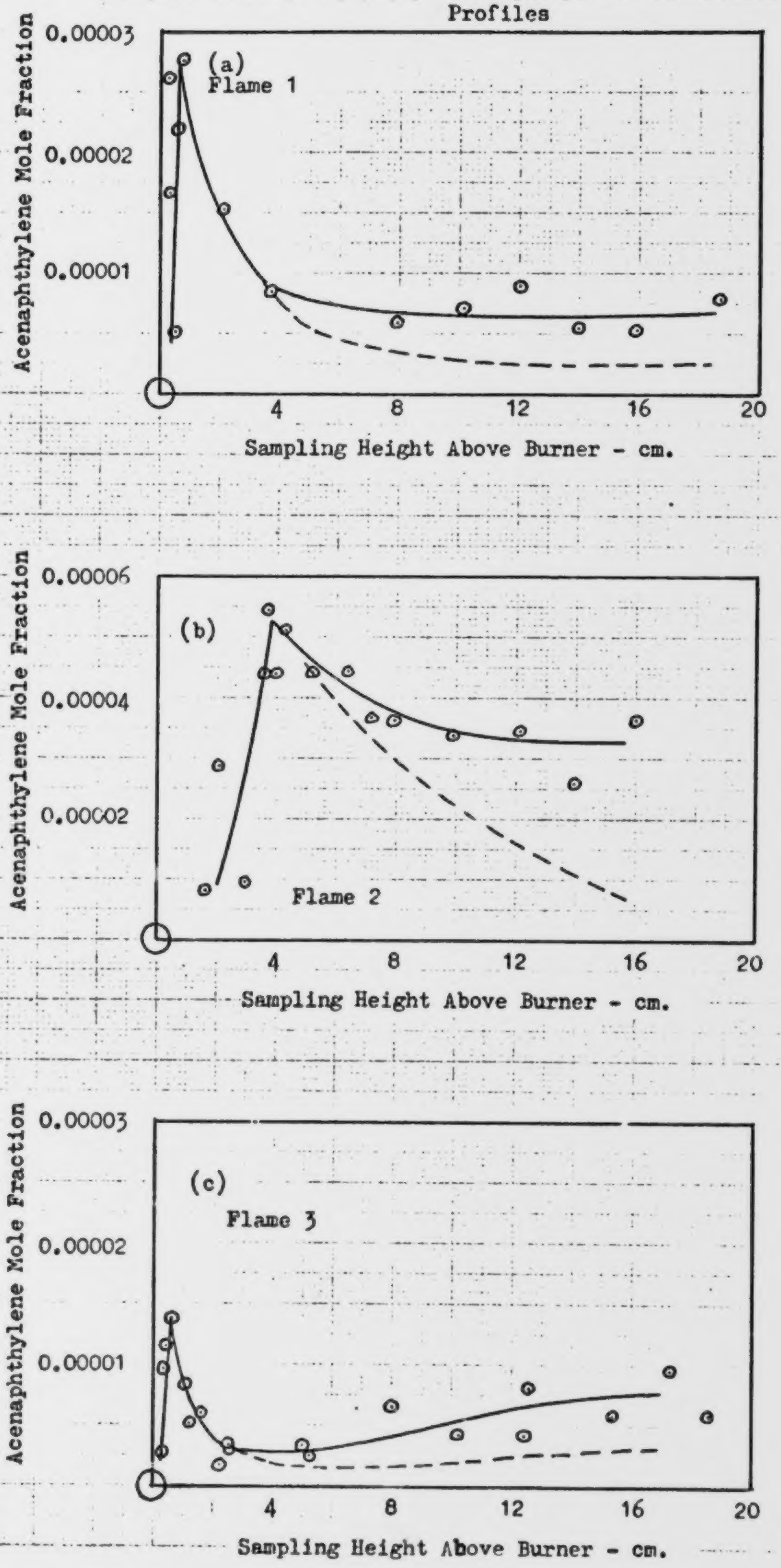


Figure 4.4.2.3.5 (a)-(c) Fluorene Concentration Profiles

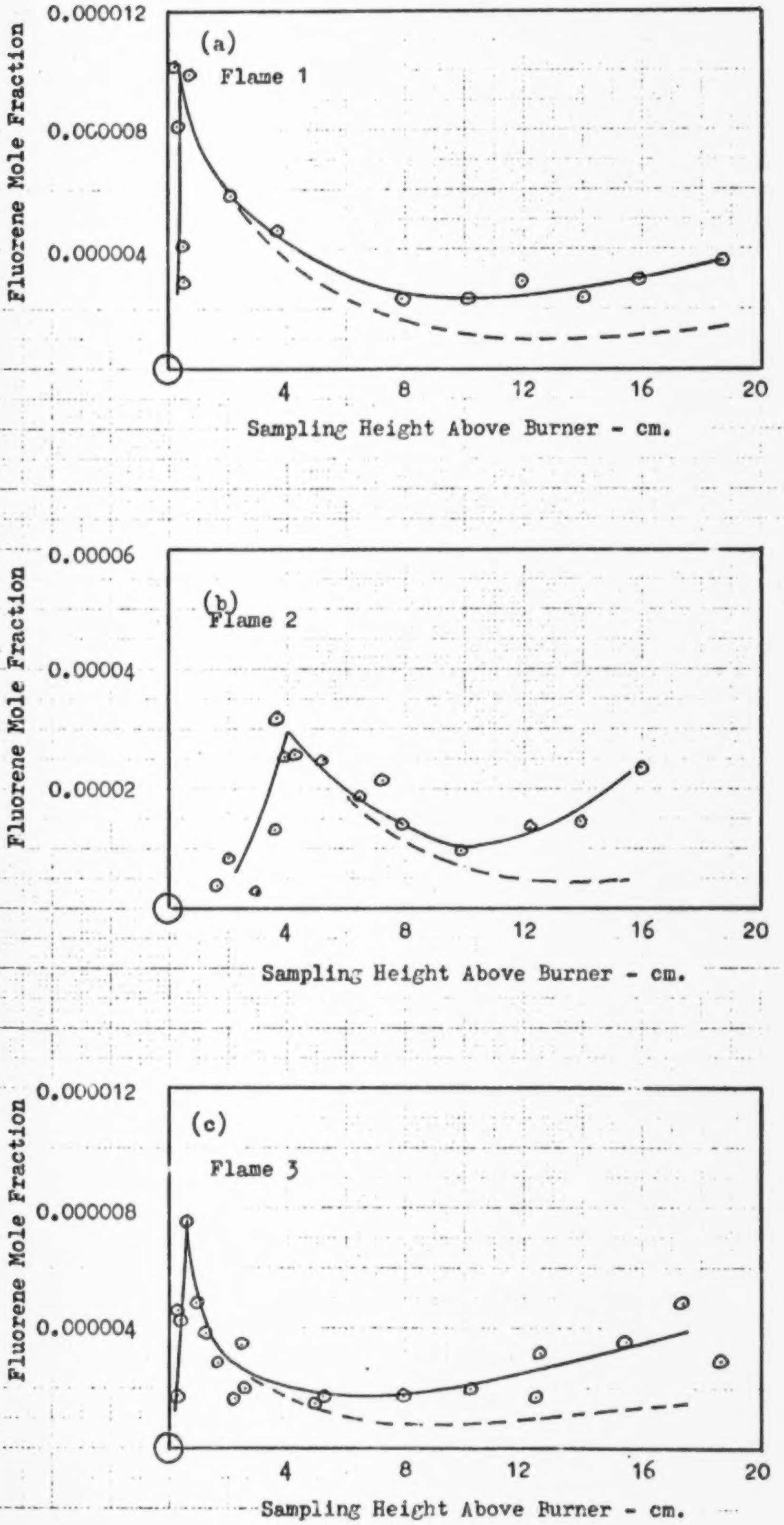


Figure 4.4.2.3.6 (a)-(c) 1.8,4.5-bi-(etheno-)naphthalene(?) Concentration Profiles

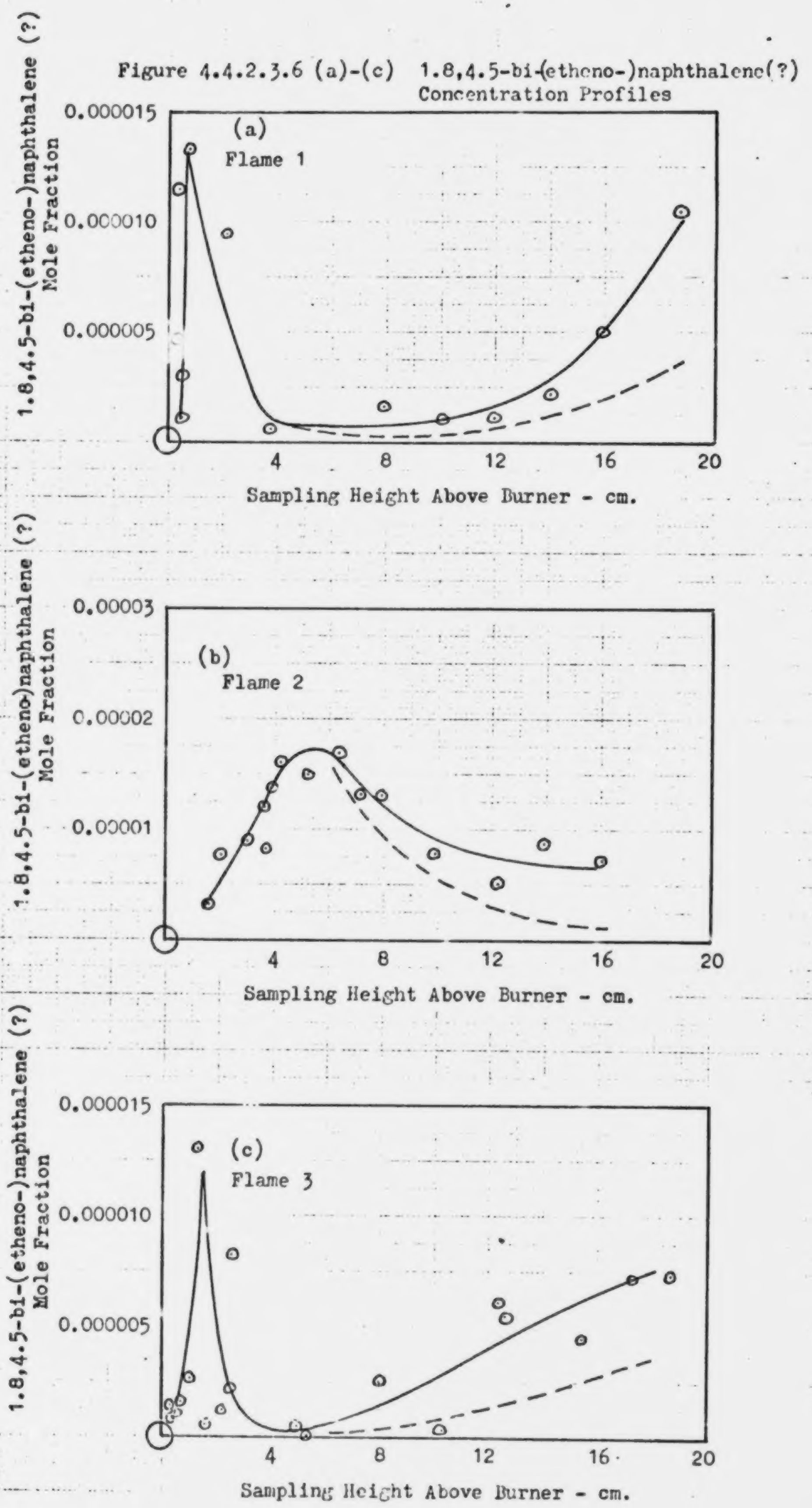


Figure 4.4.2.3.7 (a)-(c) Phenanthrene + Anthracene Concentration Profiles

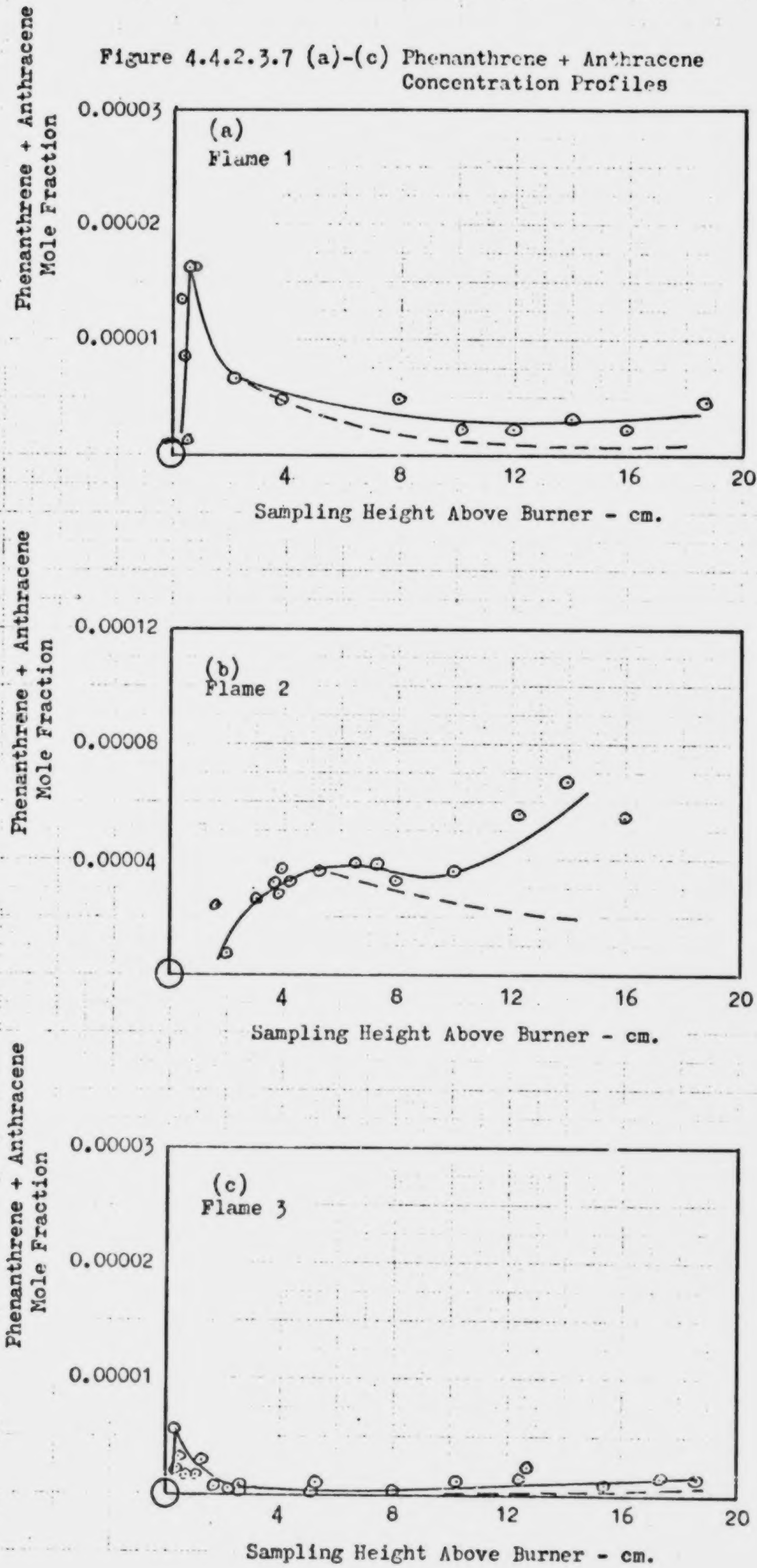


Figure 4.4.2.3.8 (a)-(c) 4.5-Methylene Phenanthrene Concentration Profiles

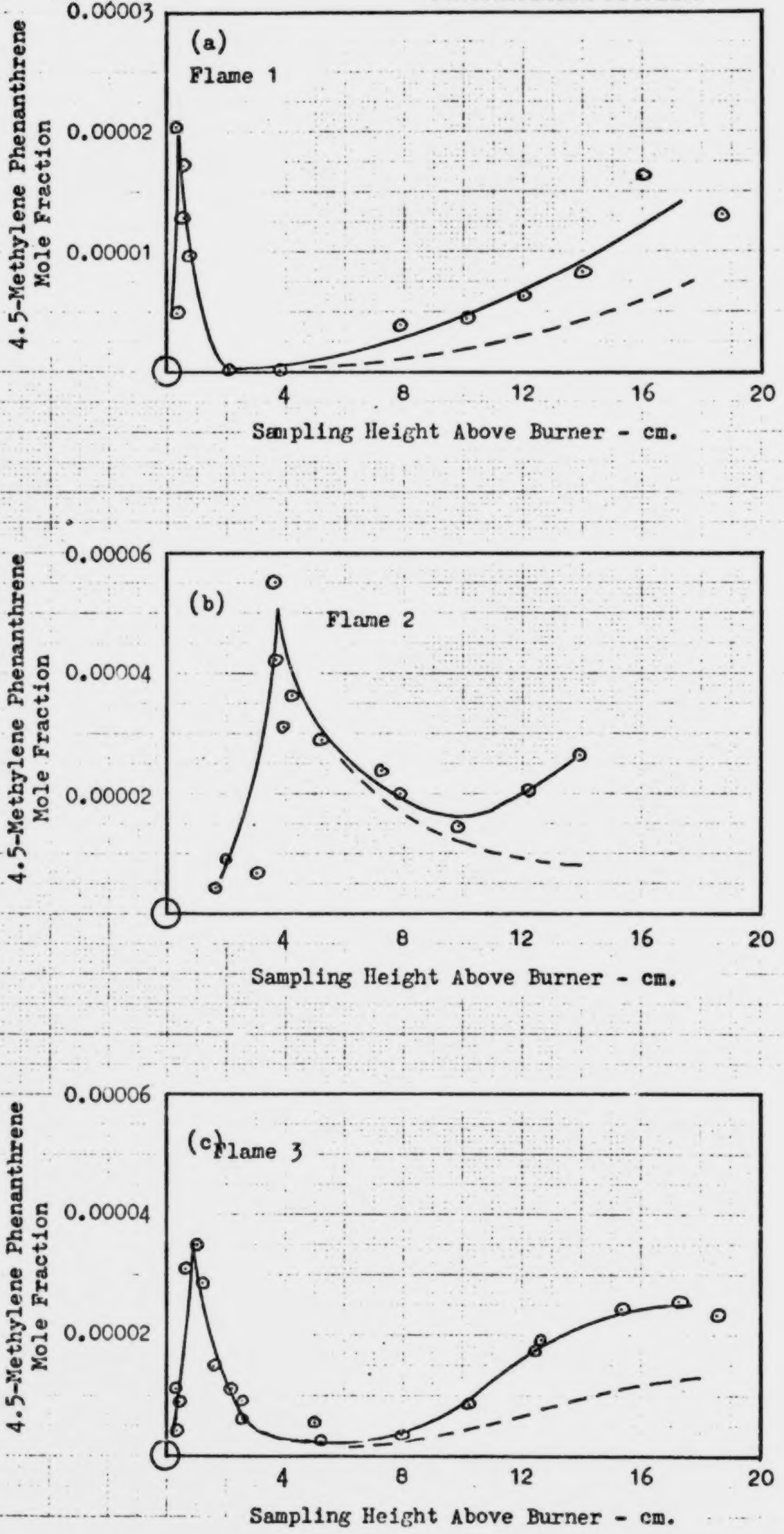


Figure 4.4.2.3.9 (a)-(c) Fluoranthene Concentration Profiles

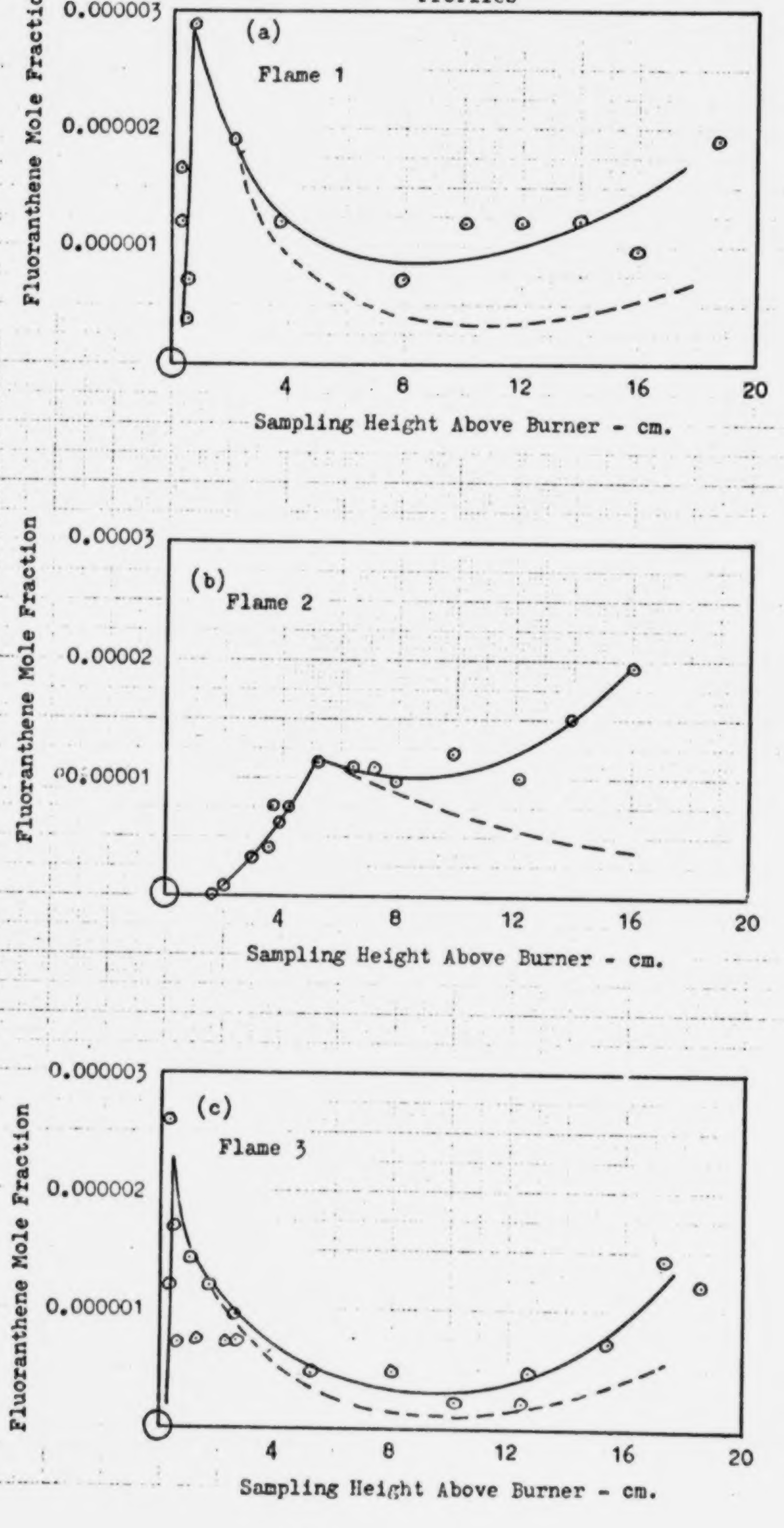


Figure 4.4.2.3.10 (a)-(c) Pyrene Concentration Profiles

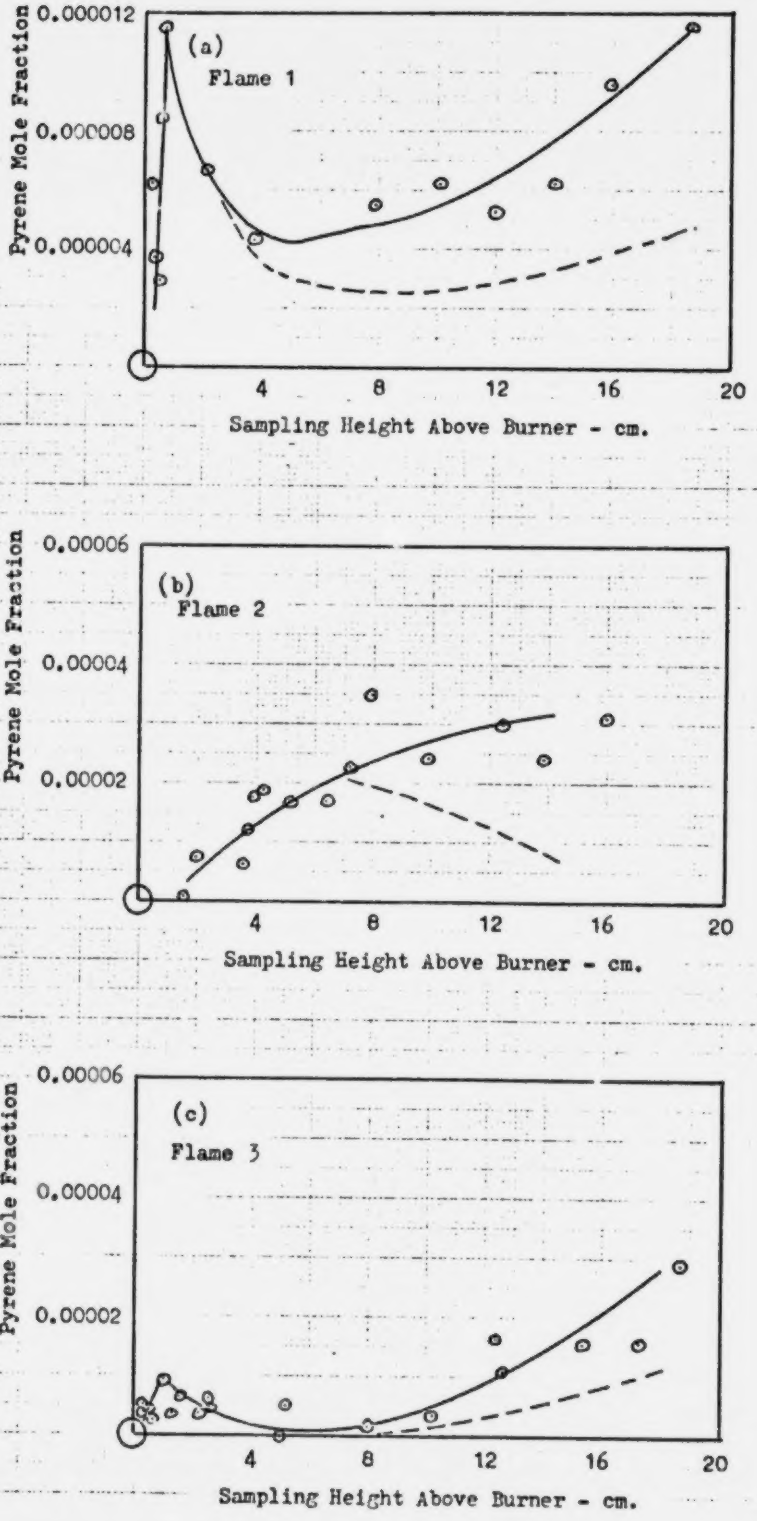


Figure 4.4.2.3.11 (a)-(c) Benzofluorenes Concentration Profiles

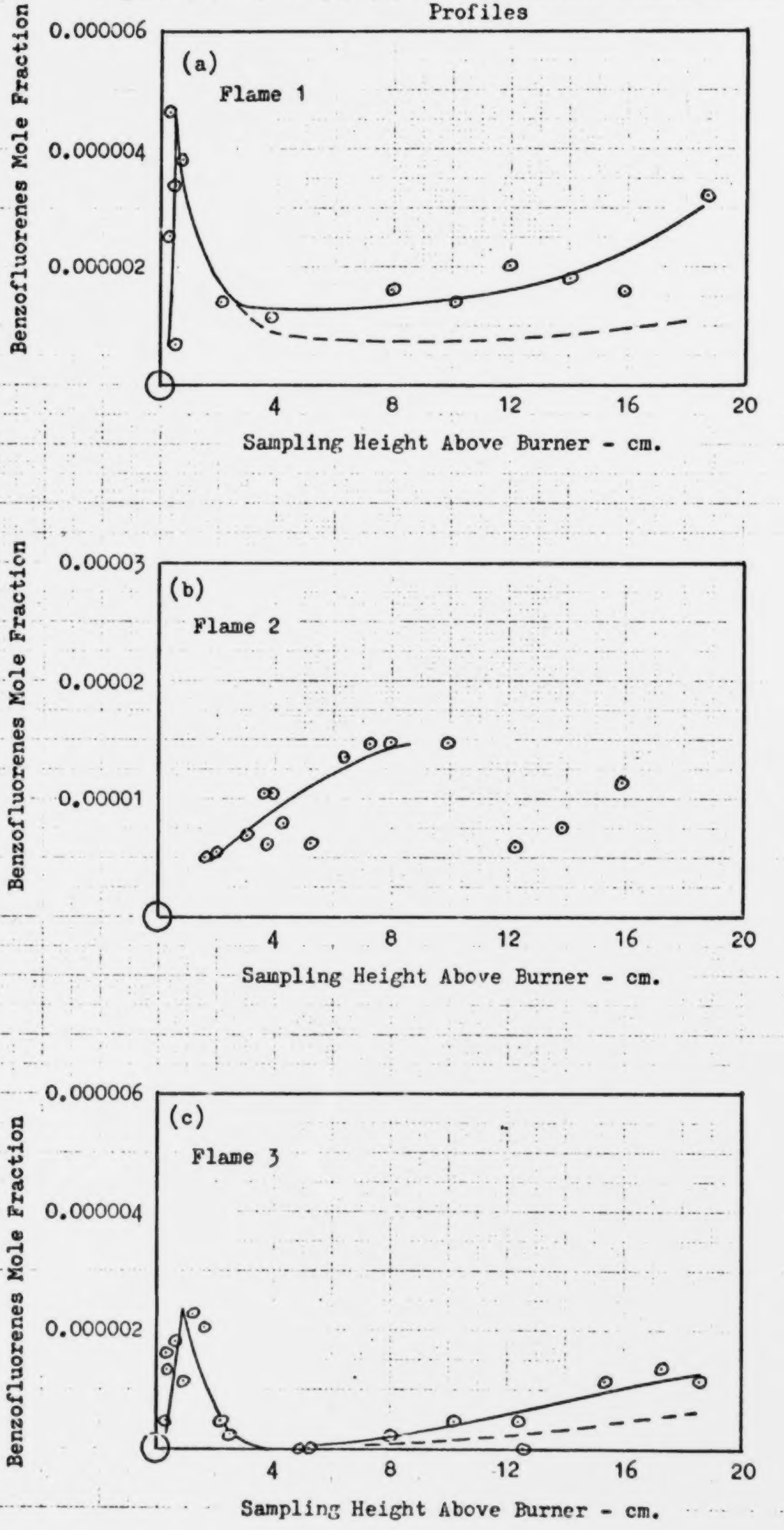
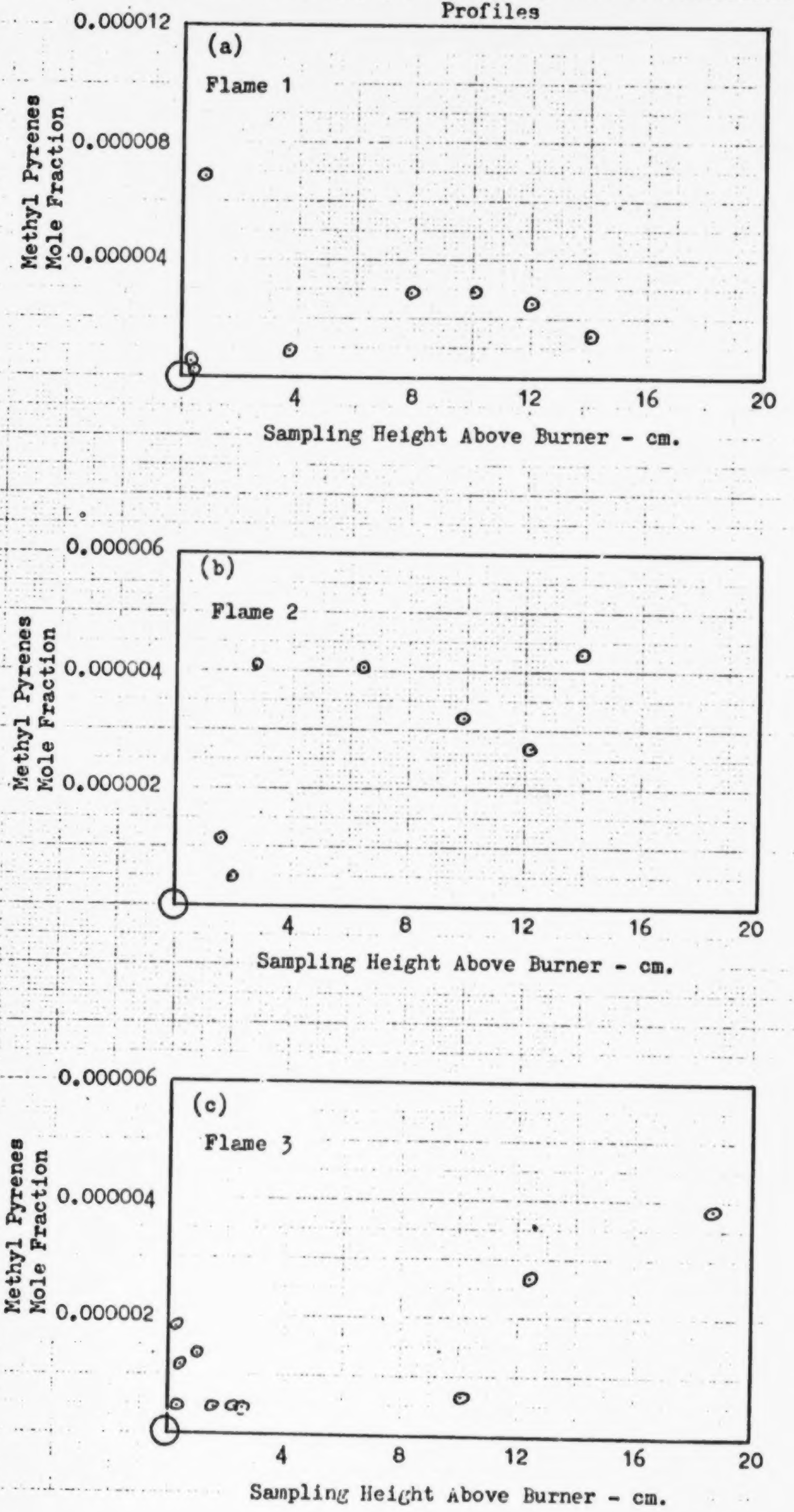


Figure 4.4.2.3.12 (a)-(c) Methyl Pyrenes Concentration Profiles



IV.4.3 Discussion of Results

Figure IV.4.3.1 gives an indication of the amount of each species formed in a typical acetylene flame (Flame 1). The mole fractions of species which are found to be present in both the 'cold' trap products and the extraction filter samples (i.e. indene, naphthalene, 1-methyl naphthalene and fluorene) have been combined. The concentration profiles which are presented in Figure IV.4.3.1 are uncorrected for the change in flame gas density high above the burner (see Section 4.1). Nevertheless, it has been shown (earlier in Chapter 4) that several hydrocarbon species(notably methane, methylacetylene/propadiene, vinylacetylene, benzene, toluene, phenylacetylene, styrene, indene, dihydronaphthalenes (?), naphthalene, biphenyl, acenaphthylene, fluorene, 1.8,4.5-bi-(etheno-)-naphthalene, 4.5-methylene phenanthrene, fluoranthene and pyrene) do show a genuine secondary increase in formation high in the flame. A further slight increase in the concentration (mole fraction) of pcah or othr aromatic species in the yellow zone is not unexpectrd since this is the region where

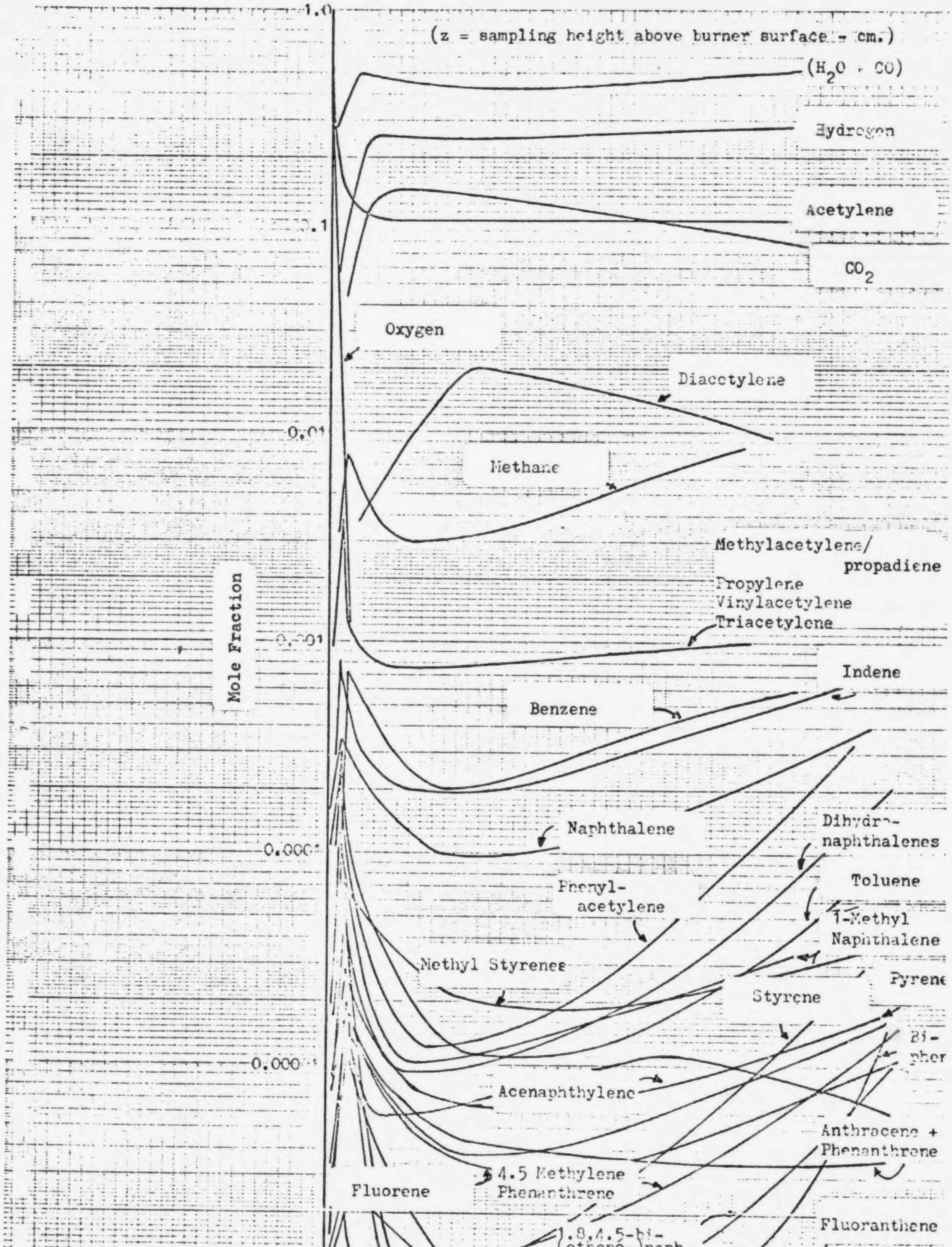
(1) the oxygen concentration (see Figures 4.3.6(a)-(d)) and the $\dot{O}H$ radical concetration (Bonne et al[35]) are zero.

(2) the acetylene concentration is still relatively high. (mole fraction ~ 0.1, see Figures 4.3.3(a)-(d)).

(3) the temperatures are favourable to pcah formation (see Figures 4.2.1 and 4.2.2 and Reference 44).

Although the secondary increase in concentration of a species such as phenylacetylene might appear large (~ 0.00001-0.001 mole fractions)

Figure IV.4.3.1 Composite Plot of Mole Fractions of All Species in Flame 1 (uncorrected for flame geometry)



such an increase would have a negligible effect on the actual acetylene concentration profile since the mole fraction of this latter species is relatively so much higher (~ 0.1). It may be postulated, therefore, that although the acetylene concentration profiles generally do not show an observable downward trend in the yellow zones of the flames considered, acetylene pyrolysis probably accounts for the secondary increase in the formation of aromatic species and pcah. (It is worth noting at this stage that the apparent secondary increase in flux of chloroform-soluble material and pcah (see Figures 1.7 and 1.9) in rich premixed oxy-acetylene flames as reported by Tompkins and Long[2] may well be due mainly to the contraction of flame gases upon cooling) In general, the concentrations of species found in equivalent oxy-ethylene flames are similar in value to those of species found in oxy-acetylene flames; however the concentration profiles are somewhat different owing to the different geometry of the oxy-ethylene flames.

A comparison between the flux fractions of species presented by Tompkins and Long[2] and the mole fractions of species presented in this study can be made since at the points of maximum and minimum concentrations

$$G_i = f_i \quad \text{(see Appendix II)}$$

where G_i is the flux fraction of species i

and f_i is the weight fraction of species i
(the weight fraction of species i is derived from the mole fraction of species i).

Although the flames studied are not identical (either in flowrate or in operating pressure) a comparison has been made between Flame 3 of this study and a hypothetical flame (between 1 and 2 in Tompkins and Long's study) which has been corrected to a total flow of premixed gases of 6.84 litres/min. (from 9.53 litres/min.).

From the results of Tompkins and Long[2] the maximum flux of the following typical species have been calculated:

Species	Actual Measured Flux (Total Flow 9.53 l./min. @ NTP) $\mu g/cm^2$ hr.	Corrected Flux (Total Flow 6.84 l./min. @ NTP) $\mu g/cm^2$ hr.
acenaphthylene	120	86
anthracene + phenanthrene	100	72
pyrene	130	94

The total mass flux of species through this hypothetical flame (assuming a uniform cross-sectional area) is 4×10^6 $\mu g/cm^2$ hr. Therefore the maximum flux fractions of acenaphthylene, anthracene + phenanthrene and pyrene are 22×10^{-6}, 18×10^{-6} and 24×10^{-6}, respectively.

In this study the maximum mole fractions of acenaphthylene, anthracene + phenanthrene and pyrene are 34×10^{-6}, 6×10^{-6} and 10×10^{-6}, respectively. Assuming an average molecular weight of species in the flame to be 25 (reasonable since the flame gases are composed mainly of the permanent gases), then the maximum weight fractions of acenaphthylene, anthracene + phenanthrene and pyrene are approximately 204×10^{-6}, 42×10^{-6} and 60×10^{-6}, respectively. A comparison between the maximum flux and weight fractions is set out below:

Species	Max^m Flux Fraction (Tompkins and Long[2])	Max^m Weight Fraction (this study)
acenaphthylene	22×10^{-6}	204×10^{-6}
anthracene + phenanthrene	18×10^{-6}	42×10^{-6}
pyrene	24×10^{-6}	80×10^{-6}

Although the maximum flux and weight fractions are comparable for anthracene + phenanthrene and pyrene, considering the errors in measuring such low quantities, the relatively high value for the maximum weight fraction of acenaphthylene indicates the necessity to collect the vapours as well as the soot from flames; much of the acenaphthylene would be lost in the collection method employed by Tompkins and Long. One interesting significance of the similarity between the maximum flux and weight fractions of anthracene + phenanthrene and pyrene is that the former was obtained from the weight of species extracted from soot and the latter was obtained from the weight of vapours condensed from a rich premixed flat oxy-acetylene flame. This suggests that pcah species may be adsorbed onto the surface of soot or 'carbon' particles upon sampling by relatively inefficient devices[2]; this is in fact supported by the results of Homann et al[1,43] since these workers have found that when 'carbon' (collected from rich premixed flames) is heated in a vacuum the residue is found to be practically pure carbon, indicating that all the hydrogen is bonded to relatively small hydrocarbon compounds.

Although only relatively stable species are analysed from the samples withdrawn from flames using the techniques described in Chapter 3, undoubtedly the blue oxidation zone represents a region where many free-radical species are present. With the present techniques one can only speculate about the sequence of events from the nature of the stable compounds found, but this does not imply that the actual reactions are not free-radical in nature.

It is most probable that no single mechanism can account for either pcah formation or 'carbon' formation in rich premixed flames although there are certain significant observations that can be made from both the results of this study and those of other workers.

It cannot be said with certainty that all unoxidised fuel molecules are initially broken down to acetylene although several workers[33,39,56] have found relatively large amounts of this compound in flame gases: (In fact acetylene is produced commercially by the partial combustion of methane with subsequent quenching (BASF, formerly called Sachsse, process)). The fact that in the oxy-ethylene flames employed in this study the ethylene concentration falls very rapidly to a very low value in the blue zone whilst the acetylene concentration rises (see Figures 4.3.3(b)+(d) and Figures 4.3.4(a)+(b)) shows that a large percentage of the original ethylene fuel is converted to acetylene (most probably via free-radical reactions); in high temperature pyrolysis experiments carried out on ethylene (e.g. in shock tubes), acetylene is generally a major product. The low temperature ($\sim$ 600–1000°C) pyrolysis of ethylene generally yields species such as 1-butene, 1.3-butadiene and cyclo-olefins. None of these compounds has been identified in the present work, although it may be argued that the inability to detect a species may imply that this species is too reactive to be sampled by the techniques employed. This argument may be refuted in the present case, however, since by using such sampling techniques it has been shown possible to detect and estimate (with a certain degree of experimental scatter) such species as diacetylene, triacetylene and tetra-acetylene (7) which themselves are known to be extremely reactive.[159-161] Thus, it may be concluded that ethylene and other olefinic species such as 1.3-butadiene are not important species in the formation of pcah in rich premixed flames.

Ethylene may be consumed initially both by pyrolysis-type reactions as the temperature rises and also by combustion since this is the region in the flame where oxygen and OH radicals are present.

The presence of methane, particularly in the blue oxidation zones of oxy-acetylene and oxy-ethylene flames, shows that some of the fuel is also broken down into C_1 units. These species, again, may be the result either of the combustion reactions or of pyrolysis-type reactions. One significant result of this study and that carried out by Fenimore et al[33] is that there is a much greater formation of methane in oxy-ethylene flames than in equivalent oxy-acetylene flames. Cullis et al[48] have presented a reaction scheme which suggests that methane may be formed by the dehydrogenation of polymeric groups during the pyrolysis of acetylene. This may well explain the presence of methane in an acetylene flame but it would not account for increased methane formation in an ethylene flame even if all the ethylene were converted initially to acetylene. One explanation may be that methane is formed to a greater extent in the combustion reactions in ethylene flames than in the combustion reactions in acetylene flames.

Since it seems very likely that some (~ 25%) of the ethylene fuel is converted to acetylene in the blue zone of rich premixed flames the fate of this latter compound must be studied. Acetylene can polymerise to benzene but the relatively low reactivity of benzene suggests that it is a stable by-product rather than a precursor of condensed-ring aromatic hydrocarbons. A very small amount of biphenyl in the flames studied suggests, however, that some benzene pyrolysis does occur probably via phenyl radicals. (Terphenyls have not been detected in this study).

Chain-lengthening processes are evident in this and in previous studies[39]. The identification of any individual polyacetylene is unambiguous by mass spectrometry since identification by 'mass measurement' is 100% positive. Although Homann and co-workers[39] report the presence of polyacetylenes up to the twelve carbon compound $C_{12}H_2$, in the present study it is likely that polyacetylenes of a higher order than C_8H_2 cannot be detected since:-

(1) they are too reactive

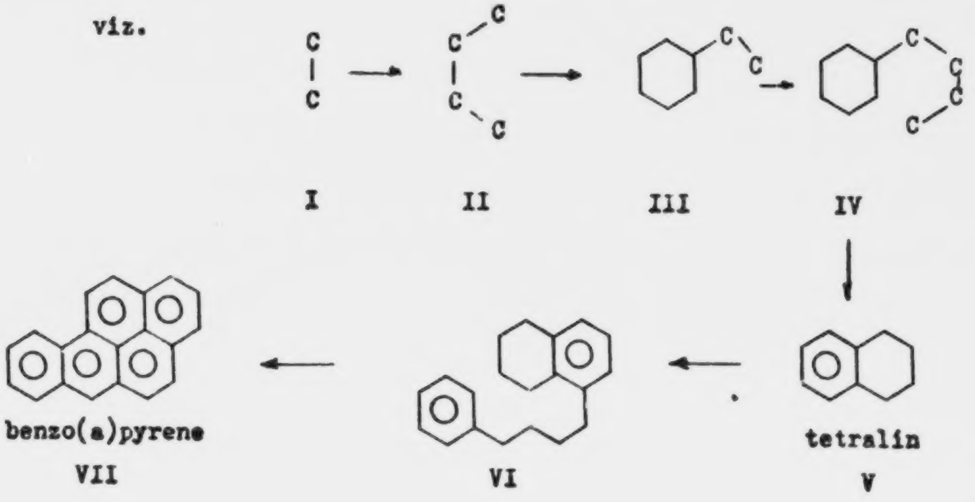
(2) they are present in too low concentrations

The polymeric nature of the chloroform-insoluble material collected low (1.3-1.9 cm.) in rich premixed oxy-acetylene flames[2] may well be accounted for by the polymerisation of one or more polyacetylenes; Homann[45] has pointed out how such reactions together with the addition of acetylene can account for the H/C ratio of approximately unity for this 'carbon' (see Section 1.1.4).

The mechanism of the formation of polyacetylenes has not been studied in detail except in the special case of diacetylene. This compound is very often formed in preference to vinylacetylene as a product during the high temperature pyrolysis of acetylene; the results of the present and other studies[39] have shown that in rich premixed hydrocarbon flames vinylacetylene is, in fact, formed prior to diacetylene and that the concentration of the latter increases whilst the concentration of the former is decreasing. This suggests that at the high temperatures prevalent in the blue zone of oxy-acetylene and oxy-ethylene flames dehydrogenation of vinylacetylene is occurring. By analogy, one might propose that triacetylene and tetra-acetylene are formed by the dehydrogenation of transitory unsaturated aliphatic compounds (or radicals) with the formulae C_6H_6 and C_8H_8, respectively, which have been formed by the polymerisation of acetylene. The species (radical) C_6H_6 could cyclise to form benzene whilst the species (radical) C_8H_8 could cyclise to form styrene. Whilst it has been shown[246] that an equilibrium exists at relatively high temperatures between styrene, phenylacetylene and hydrogen, it has been claimed that phenylacetylene may be prepared at relatively low temperatures (~ 100°C) from diacetylene[251].

The presence of C_6-C_2 species such as phenylacetylene and styrene is of particular interest since this type of compound has been postulated by Badger and co-workers[62,63] as being important in the step-wise synthesis of pcah from a C_2 species during hydrocarbon pyrolysis.

viz.



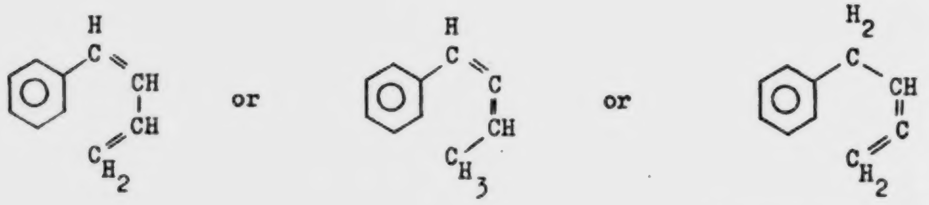
I II III IV

tetralin V

VI

benzo(a)pyrene VII

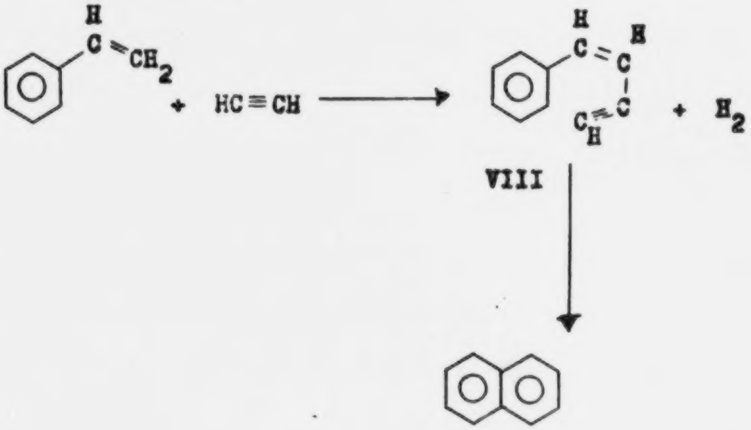
The next stage (after the C_6-C_2 species) in the step-wise synthesis is postulated to be a C_6-C_4 species (IV) which could well be a phenylbutadiene or related radical.



phenylbutadienes

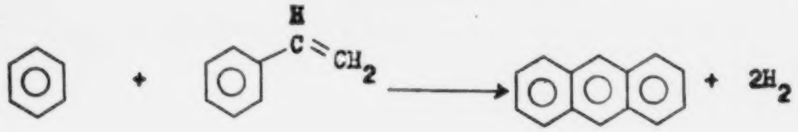
A species whose molecular weight is equal to 130 (that of phenylbutadiene) has been detected in the present work, although its identification is not certain (however, its formula is $C_{10}H_{10}$). It is possible, however, that phenylbutadiene (or its related radical) might stabilise as a dihydronaphthalene upon sampling since naphthalene has been prepared from phenylbutadiene by passing this compound through red-hot tubes[247]. In Badger's reaction scheme compound V may therefore be a dihydronaphthalene rather than tetralin (a tetrahydronaphthalene), especially in flames where dehydrogenation reactions are favoured. No tetralin has been detected in the present studies of flames. Groll[46] has proposed that naphthalene may be formed indirectly from acetylene via a dihydronaphthalene (see Section 1.2.1).

Stehling and co-workers[112] pyrolysed acetylene with styrene as an additive to find that there is a slight increase in naphthalene formation at 800°C, thus suggesting that the following overall reaction (cf. Badger et al[62,63]) may be occurring:



VIII

Many years ago, Berthelot[252] synthesised anthracene from benzene and styrene, thus suggesting that the following overall reaction may occur:



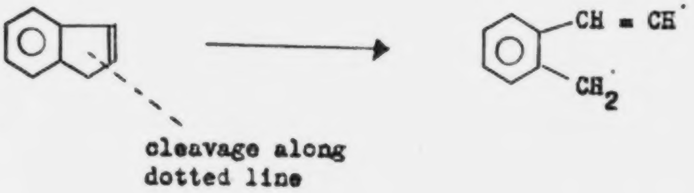
The presence of phenylacetylene is not unknown in products of incomplete combustion or in products of pyrolysis-type experiments, particularly in the case of benzene.

(1) In rich premixed benzene/oxygen flames Homann and co-workers[39] have found that the concentrations of species such as phenylacetylene, indene, methyl naphthalene and biphenyl pass through maxima and decrease in the burned gases of the flames. Acetylene and polyacetylenes are formed also in such flames.

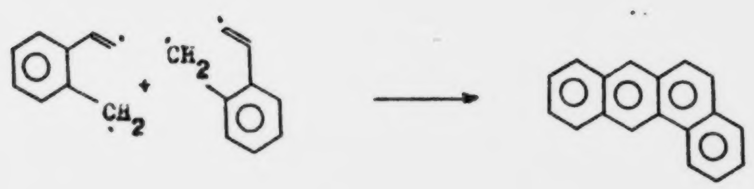
(2) Very recently, Kern and Spengler[16] have reported the presence of both phenylacetylene and styrene (in roughly equal concentrations) in the products formed in hexane diffusion flames.

(3) Using an electric arc in benzene, Müller and Bänninger[253] have found evidence for the formation of phenyl and acetylenyl radicals since the products include (apart from 95% unreacted benzene) phenylacetylene, biphenyl, diacetylene (and some higher acetylenes) together with hydrogen and acetylene.

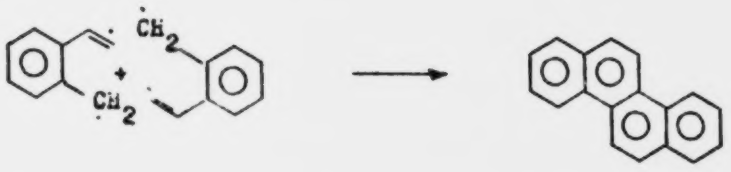
The initial breakdown of fuel (both acetylene and ethylene) into C_1 species, which has been mentioned previously, may account for the formation of species with odd numbers of carbon atoms, e.g. toluene, indene, and 1-methyl naphthalene. The possible importance of indene in the formation of higher molecular weight aromatic species in flames has been suggested by Davies and Scully[254]. These workers have found that when indene is injected into a rich towns gas/air premixed flame, soot formation is strikingly high and they have suggested that the following reactions might occur:



This radical may also be formed by the dehydrogenation of o-methyl styrene, a species which has been suggested to be present in the flame gases of rich oxy-acetylene and oxy-ethylene flames in the present work. (see Section 4.4.1.2). Davies and Scully[254] have also proposed that benz(a)anthracene and chrysene might be formed from the above-mentioned diradical in the following manner:



benz(a)anthracene



chrysene

These workers have also reported that when styrene is added to the towns gas flame instead of indene, much less soot is formed indicating that the CH_2 group in the radical obtained from indene plays an important rôle. This is supported by the fact that the soot yield with styrene is also less than that with toluene[254].

Davies and Scully have concluded that in such flames,

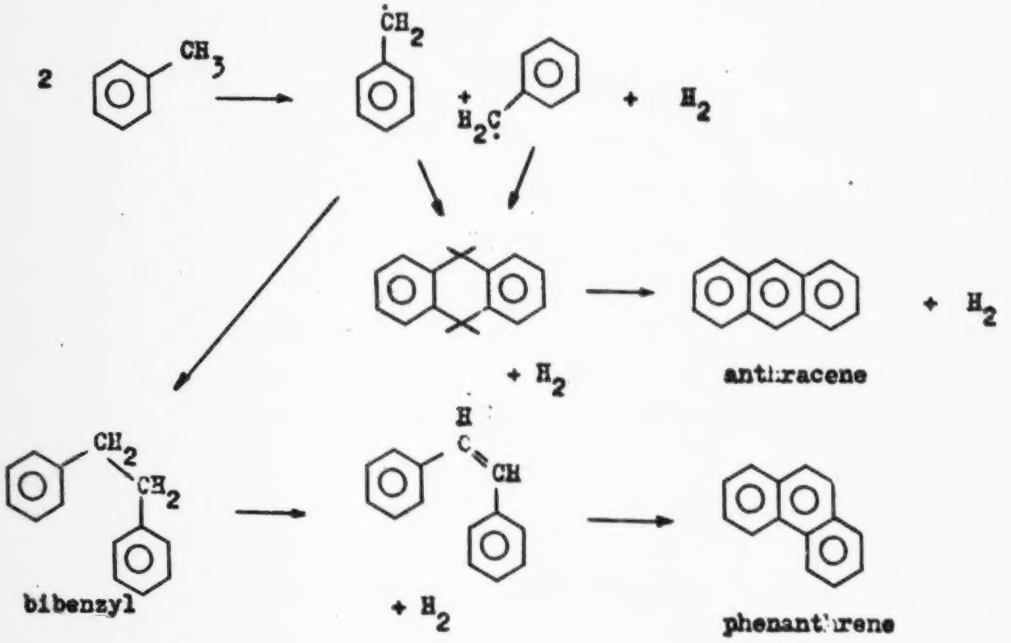
(1) benzene rings favour soot formation

(2) attached methyl groups promote soot formation even further

(3) polycondensed aromatic hydrocarbons favour soot formation.

Point (2) is supported by the results of Stehling and co-workers[112]; these workers have found that in the pyrolysis of acetylene the rate of disappearance of this compound is accelerated by the addition of 2-methyl naphthalene. However, toluene does not appear to affect the rate of acetylene disappearance.

Daniels[255] has concluded from the results of Street and Thomas[38] that in premixed flames alkyl groups attached to benzene rings increase the amount of oxygen required to suppress 'carbon' formation. This may be due to the participation of side-chains in ring-closures yielding pcah in the flames, thus giving rise to compounds from which it is difficult to suppress 'carbon' formation. Lang, Buffleb and Zander[157] report that the pyrolysis of alkyl substituted aromatic hydrocarbons occurs via direct nuclear condensation, the primary bonding occurring across the alkyl group. Kinney[151] has suggested, for instance, that toluene can condense to bibenzyl which in turn may produce anthracene or phenanthrene.



No bibenzyl (mol. wt. = 182) has been found in the present work although Ingold and Lossing[256] and Blades et al[257] have shown by mass spectrometry that benzyl radicals are formed during the pyrolysis of toluene (which has been found in both oxy-acetylene and oxy-ethylene flames).

Homann and Wagner[1] have suggested that polycyclic aromatic hydrocarbons such as anthracene, phenanthrene, pyrene, etc. (i.e. the so-called Group 2) cannot be important intermediates or 'nuclei' in the formation of 'carbon' in acetylene flames since the rate of 'carbon' formation decreases to zero whilst the concentration of these species increases. (From their results on the pyrolysis of benzene Sakai et al[154] have concluded also that 'bare aromatic' molecules cannot be intermediate compounds in the formation of coke or tar in the pyrolysis of petroleum hydrocarbons at temperatures around 800°C.) The results of the present study show, however, that the concentrations (mole fractions) of most poah do not rise steadily in the burned gas; instead the mole fractions of several poah increase to maximum values in the blue zone, then fall to low but definite values in the burned gas. Similar results, using a different and less satisfactory sampling technique, have been obtained by previous workers[2].

There is no evidence in the present study for the presence of the so-called "Group 3" hydrocarbons[1] (reactive poah with side chains and containing more hydrogen than the parent poah) in the blue zones of oxy-acetylene and oxy-ethylene flames, although it should be pointed out that the concentration of an individual species within this group is of the order of 10^{-7} of a mole fraction. Although Homann and Wagner[258] consider Group 3 species "to be important intermediates for the formation of solid particles" in rich premixed flat flames, there is some uncertainty as to the lower mass number limit of this Group, since this has been reported as being ~150[1], ~90[259], and 250[258]. Group 3 hydrocarbons have been claimed to be detected by mass spectrometry both by evaporating soot samples in vacuo and also directly from the flame, thus suggesting that such molecules are relatively stable species.

It is difficult to understand how Homann and Wagner[1] could stress the possible importance of this group of compounds in 'carbon' formation and not to comment on the presence of species such as phenylacetylene, styrene, etc., which have been shown (in the present work) to be present in relatively appreciable quantities. Homann and co-workers[39] have shown, however, that species such as phenylacetylene are present in rich premixed benzene/oxygen flames and that the concentration profiles of such species are similar to those found (in the present work) in similar rich premixed oxy-acetylene flames.

IV.5. CONCLUSIONS

IV.5.I. Sampling Techniques and Analysis

The results of this investigation demonstrate that by the use of high resolution mass spectrometry and programmed-temperature gas-liquid chromatography, it is possible to detect a stable species whose mole fraction in the flame gases is approximately 10^{-6}, thus obviating the necessity for a complex molecular beam sampling/mass spectrometer system as has been used previously by Homann et al[39] on work of a similar nature. These workers have shown, however, that such a system does enable the concentrations of a few free-radicals to be determined.

A technique has been devised for using the GEC-AEI MS9 mass spectrometer as a quantitative instrument by admitting into the combustion chamber (along with the premixed gases) a known flowrate of an inert reference gas (argon).

Programmed-temperature GLC techniques have been shown to provide a rapid and efficient means of separation and determination of polycyclic aromatic hydrocarbons and other compounds which have been identified. A technique has been employed to provide an efficient means of collecting gas chromatographic fractions for the identification of species by both mass spectrometry and UV absorption spectroscopy. It has been found necessary to use both of these latter techniques for the identification of certain species present in the flame gases.

The similarity between the present batch results and those results reported by the only previous workers in the field[39] confirms that sampling via quartz microprobes in the manner described is efficient in terms of reaction quenching. The results of this study indicate, also, that such microprobes sample species which are present in the gaseous phase rather than associated with the solid phase ('carbon') thus suggesting that a large proportion of the pcah are adsorbed onto the surface of 'carbon' particles when this material is withdrawn from flames[2].

IV.5.II. Formation of Polyacetylenes

The presence of polyacetylenes in rich premixed oxy-acetylene and oxy-ethylene flames has been confirmed but, because of their relatively high reactivity, concentration profiles cannot be determined very accurately. It cannot be established whether equilibria exist between these compounds and hydrogen as Bonne, Homann and Wagner[35] have suggested.

It is difficult to propose a mechanism which accounts for the formation of high molecular weight polyacetylenes although as Homann and Wagner[1] have pointed out, such a mechanism is probably free-radical in nature. It is possible that polyacetylenes are formed by the dehydrogenation of polymers with the generic formula $(C_2H_2)_n$; these species are most probably free-radical in nature. When x = 2 the polymer (radical) may stabilise as vinylacetylene or be dehydrogenated to diacetylene; when x = 3 the polymer (radical) may either stabilise as benzene (cyclisation) or be dehydrogenated to triacetylene, etc. It is not proposed that such polymers are formed by the direct polymerisation of acetylene but rather by the combination of acetylenyl and polyacetylenyl radicals.

IV.5.III. Polycyclic Aromatic Hydrocarbon Formation

The concentration (mole fraction) profiles of pcah throughout the flame support, in general, the results obtained by Tompkins and Long[2] whose sampling technique was never claimed to be other than relatively crude. The results of the present study and those reported by Tompkins and Long show that, in general, the concentrations of individual pcah do not rise steadily in the burned gas (yellow zone) of either oxy-acetylene or oxy-ethylene flames. Thus some doubt must be cast upon the validity of those results reported by Homann and Wagner[1] which suggest that they do.

With the exception of species such as toluene, phenylacetylene, styrene, methyl styrenes (?), 1-methyl naphthalene, methyl pyrenes, etc., there is little evidence for the presence of many alkyl substituted pcah in either the blue or yellow zones of rich premixed oxy-acetylene and oxy-ethylene flames. There is no evidence of the so-called 'Group 3' hydrocarbons that Homann and Wagner[1] have claimed are formed in and are destroyed by the end of the blue zones of such flames although these species may be present in concentrations of less than 10^{-6} mole fractions.

The presence of several significant compounds such as phenylacetylene, styrene and the compound whose molecular weight is 130 is particularly interesting since this suggests that the reaction mechanisms proposed by Badger and co-workers[62,63] may well account, at least in part, for the formation of pcah from the two-carbon species, acetylene. It is unlikely, however, that such reaction schemes solely account for the formation of higher molecular weight pcah in rich premixed flames since once formed, pcah may be pyrolysed to give higher aromatic species as is indicated by the results of Lang, Buffleb and Zander[157].

IV.5.IV Concentration Profiles

With a few exceptions, the concentration (mole fraction) profiles of many species in rich premixed oxy-acetylene and oxy-ethylene flames are similar. The typical profile may be divided into three parts as follows:

(a) The initial rapid formation of the species in the pre-heat zone and in the less-hot part of the blue oxidation zone; this probably involves the pyrolysis of low molecular weight species in the presence of oxygen and ȮH radicals. Some combustion of hydrocarbon species will also be taking place, simultaneously, of course.

(b) The destruction of some compounds to low (sometimes zero) concentrations due to combustion and oxidation reactions (presumably by attack by ȮH radicals, chiefly).

(c) The secondary increase in concentration; this most probably being due to the pyrolysis of residual lower molecular weight species, in particular acetylene whose concentration in the burned gases of all the flames studied is relatively high. The temperatures within this region are favourable to poah formation (Figures 4.2.1, 4.2.2, Ref. 44).

IV.5.V. The Importance of Acetylene and Ethylene

Apart from a few compounds (e.g. methane) the concentrations of products are similar in both oxy-acetylene and oxy-ethylene flames. This, together with the fact that relatively large amounts of acetylene are formed in oxy-ethylene flames, suggests that ethylene is first converted (in part, since some ethylene is oxidised in combustion reactions) to acetylene which is then responsible for the formation of the many products of higher molecular weight found in both types of flame.

No (or at least, relatively very little) ethylene, 1.3-butadiene, 1-butene, etc. are present in the rich premixed oxy-acetylene and oxy-ethylene flames, thus suggesting that the following mechanism does not occur in flames:-

ethylene ⟶ 1.3-butadiene ⟶ products

(However, this does not rule out the possibility that such a mechanism might possibly account for the formation of poah in pyrolysis experiments where the degree of dehydrogenation is less than in flames.)

IV.5.VI 'Carbon' Formation

It has not been the intention in the present study to investigate the mechanism of 'carbon' formation although several observations are worthy of mention.

(1) The different types of 'carbon' collected at various heights in both oxy-acetylene and oxy-ethylene flames are similar in appearance to those reported by Tompkins and Long[2].

(2) The results of the present work suggest that pcah are adsorbed onto the surface of 'carbon' particles when these are collected from the flame through filters, etc.

(3) The similarity of products in both oxy-acetylene and oxy-ethylene flames suggests that 'carbon' is formed via the same mechanism in both cases.

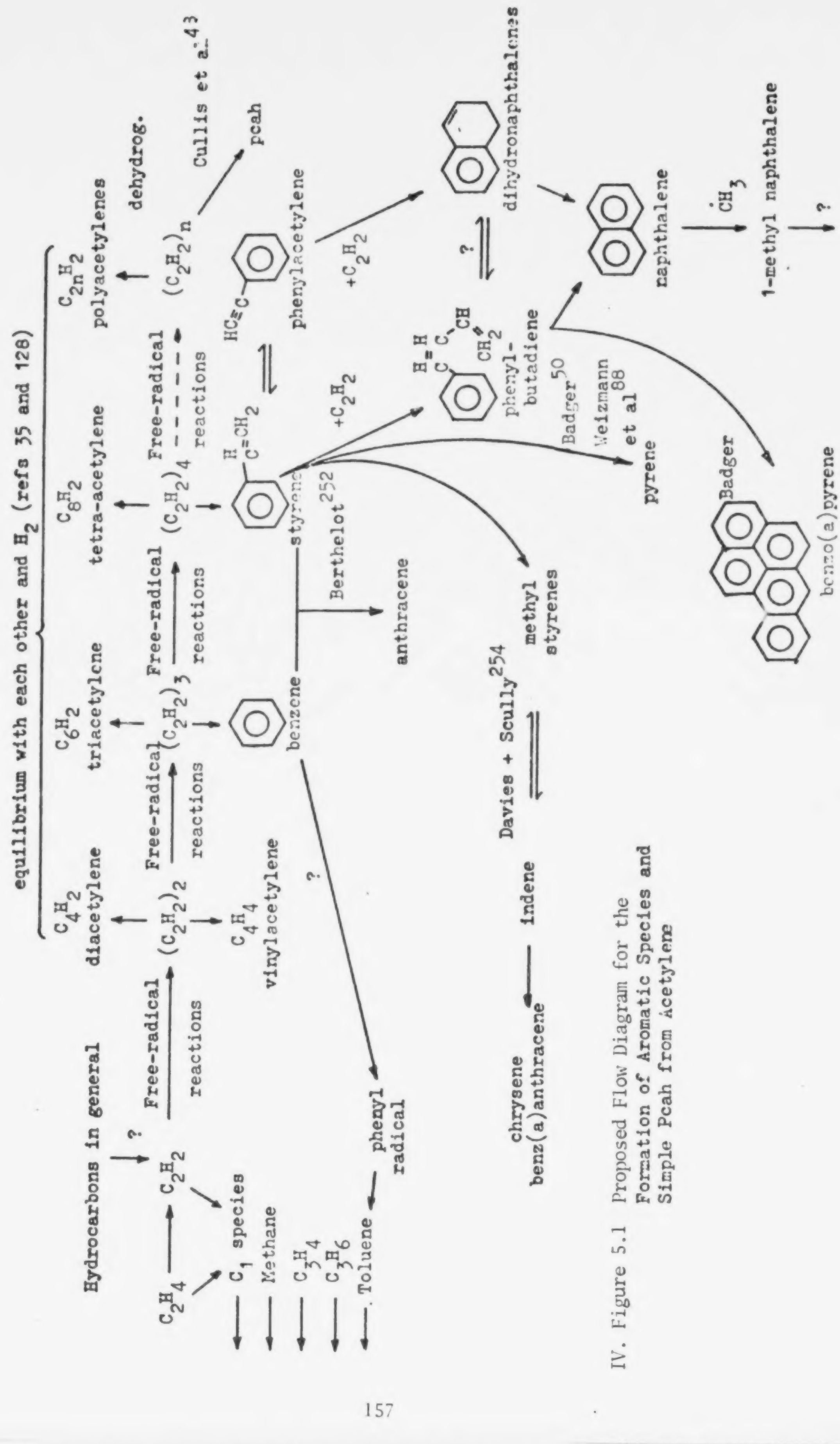
(4) From the results obtained in this study it is not possible to say whether polyacetylenes, bare pcah or other aromatic species

(with side chains) are important intermediates in the formation of 'carbon' since different mechanisms and compounds may be important at different heights in the flames. The fact that aromatic molecules with side chains tend to promote soot formation in flames (see Section 4.4.3) indicates that this type of species may play an important rôle in 'carbon' formation. However, it is most likely that, as other workers have concluded, bare aromatic species are most probably relatively stable by-products of the reactions rather than 'nuclei' for 'carbon' formation.

IV.5.VII. Mechanisms for Polyacetylene and Pcah Formation

The reaction scheme outlined in Figure 5.1 summarises the results of this study and those of others deemed to be relevant; it is apparent that a number of reaction schemes may account for the formation of pcah although some indication is given of how lower molecular weight species such as phenylacetylene, dihydronaphthalene (?) etc., are formed.

It has not been possible to establish the nature of the actual species taking part in the complex reactions involved but it seems most likely that these are free-radical in nature; thus the stable compounds identified can at this stage only give an indication of the free-radicals involved.


equilibrium with each other and H2 (refs 35 and 128)
Hydrocarbons in general
?
C2H4
C2H2
C1 species
Methane
C3H4
C3H6
Toluene
phenyl radical
Free-radical reactions
(C2H2)2
C4H2 diacetylene
C4H4 vinylacetylene
?
Free-radical reactions
(C2H2)3
C6H2 triacetylene
benzene
Free-radical reactions
(C2H2)4
C8H2 tetra-acetylene
styrene
H C=CH2
Free-radical reactions
C2nH2 polyacetylenes
dehydrog.
(C2H2)n
Cullis et al.43
pcah
HC≡C
phenylacetylene
+C2H2
+C2H2
H = H C C CH CH2
phenyl-butadiene
?
dihydronaphthalenes
naphthalene
ĊH3
1-methyl naphthalene
?
Berthelot252
anthracene
Badger50
Weizmann et al88
pyrene
methyl styrenes
Badger
benzo(a)pyrene
Davies + Scully254
indene
chrysene benz(a)anthracene

IV. Figure 5.1 Proposed Flow Diagram for the Formation of Aromatic Species and Simple Pcah from Acetylene

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Errata

The following references have been duplicated:-

Nos. 3 and 54

16 and 162

38 and 92

Part V A Brief Review of the Use of Organo-Metallic and Metal Containing Additives in Suppressing Soot and Polycyclic Aromatics in Flames

The effect of introducing oxygen into the combustion air, or into the hydrocarbon fuel itself, in a diffusion flame was studied as an early part of the present programme of work. The results emphasized the undesirability of either a general or local depletion of oxygen in the diffusion-flame combustion of hydrocarbons since this leads to an increase in the formation of polycyclic aromatic hydrocarbons, including the carcinogen benzo (a) pyrene. Oxygen enrichment of combustion air can greatly reduce the concentration of p. c. a. h. in the soot. If sufficient oxygen is added to the fuel itself, p. c. a. h. can be eliminated from the soot.

It was hoped to continue this work by examining the effects of organo-metallic additives on the formation of soot and p. c. a. h. in flames. Pyrolysis and oxidation processes are well-known to be influenced by catalysts and additives and it was hoped to attempt to reduce the formation of p. c. a. h. during flame combustion by the use of these.

Unfortunately the loss of key personnel with experience in the synthesis of metal chelates precluded the continuation of this aspect of the work.

However, recent work in Germany by G. Spengler and G. Haupt[a] has indicated that reduction in both soot and polycyclic aromatic hydrocarbons by the addition of compounds containing metals is feasible. Compound such as methylcyclopenta dienyl manganese tricarbonyl iron pentacarbonyl and ferrocene when introduced into diffusion flames of, atomized fuels, reduced soot and p. c. a. h. This interesting piece of work also claims that the formation of acetylene in the flame was in no way influenced by the additives used.

In later work, these authors studied 29 organo-metallic and certain organic compounds in a single cyclinder 4-stroke diesel engine. Methylcyclo penta dienyl manganese tricarbonyl and the iron pentacarbonyl seemed to be the most effective additives in reducing soot and p.c.a.h. whilst of the organic additives, cyclohexanol nitrate was the most effective, although less so than the metal-containing additives.

M. W. Shayeson[b] found that organo-metallic compounds of barium, maganese and iron were the most effective smoke reducing fuel additives but that the effectiveness was a function of engine design and power level. (J. P. 5. fuel was used for the tests and a jet engine was operated in a test cell).

A review of burner fuel additives by K. C. Salooja[c] has recently appeared and the author points out that despite much interest in smoke suppressants over many years, the mechanism by which these additives act, in any of the applications has not been explored.

However, also very recently, a very interesting paper by D. H. Cotton, N. J. Friswell and D. R. Jenkins[d] has appeared. They report measurements on the effects of forty metals on the amount of soot emitted by a laboratory scale propane diffusion flame. The alkaline earth metals were amongst the most effective and it will be remembered that over the last few years a number of proprietary additives containing barium compounds have been produced, and claimed to be effective as diesel fuel additives for example.

A semi-quantitative mechanism is proposed to account for the action of the alkaline earth metals: its basis is that these metals undergo a homogeneous gas-phase reaction with hydrogen or water vapour in flame gases. Hydrogen atoms so produced will react rapidly with water vapour to give hydroxyl radicals, so that the net effect of either decompostion will be to produce .OH radicals. These will then be effective in rapidly removing soot or soot precursors.

There seems to be no evidence on the effect of these additives on polycylic aromatic hydrocarbons associated with soot, but one would expect these or their precursors to be removed by .OH radicals too.

Whilst interest is being shown in soot suppressing additives, their possible toxicity as exhaust products and the effects of solid products on engine operation must always be borne in mind.

References - Part V

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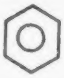
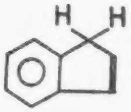
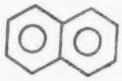
APPENDIX I Nomenclature of Polycyclic Aromatic Hydrocarbons

The nomenclature of pcah relevant to this study is given below. The names used are according to I.U.P.A.C.[20] (1957) Rules and the compounds are listed in order of increasing molecular weights (in parentneses). The symbol  is used to denote a benzene-ring configuration.

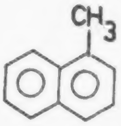
Indene (116)



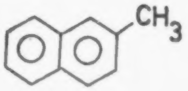
Naphthalene (128)



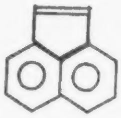
1-Methyl Naphthalene (142)



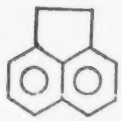
2-Methyl Naphthalene (142)



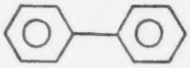
Acenaphthylene (152)



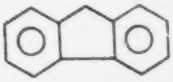
Acenaphthene (154)

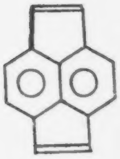


Biphenyl (154)



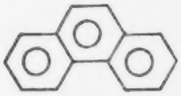
Fluorene (166)



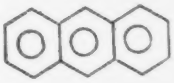


Cyclopenta (f,g) acenaphthylene (176)
[1.8, 4.5-bi-(etheno-) naphthalene]

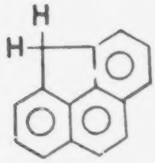
Phenanthrene (178)



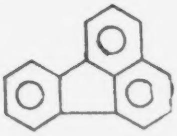
Anthracene (178)



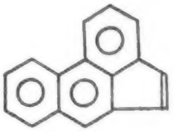
4.5-methylene phenanthrene (190)



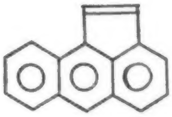
Fluoranthene (202)



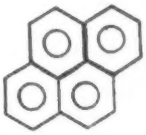
Acephenanthrylene (202)



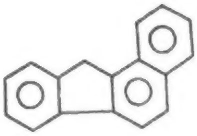
Aceanthrylene (202)



Pyrene (202)



Benzo(a)fluorene (216)



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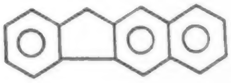

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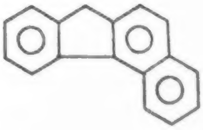
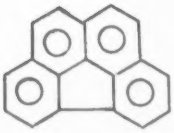
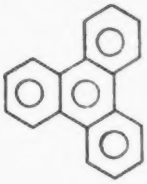


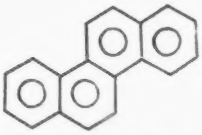
Benzo(mno)fluoranthene (226)



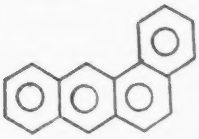
Triphenylene (228)



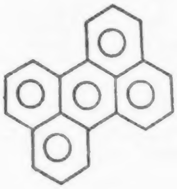
Chrysene (228)



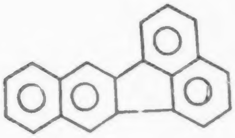
Benz(a)anthracene (228)



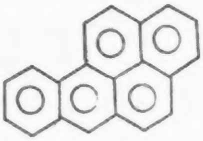
Perylene (252)



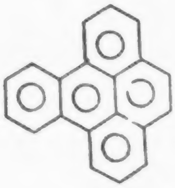
Benzo(k)fluoranthene (252)



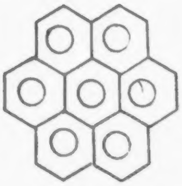
Benzo(a)pyrene (252)



Benzo(e)pyrene (252)



Coronene (300)



APPENDIX II The Flux and Concentration of a Species in a Flame

Experimental results have shown[167] that microprobes constructed according to the method described by Fristrom and Westenberg[30] sample the concentration and not the flux of a species in a simple system. Although the concentration gradients which exist in flames are much greater than those which were set up in the simple experiment by Westenberg et al[167], it may reasonably be assumed that such microprobes sample concentrations and not fluxes in flames.

Concentration

The concentration, N_i, of a species i at a point in a flame is defined as the number of moles of the species present per unit volume at the point in question. If W_i is the mass per unit volume of species i with molecular weight M_i at the point, then

$$W_i = N_i M_i$$

If ρ is the total mass density at the point, then

$$\rho = \sum_i W_i$$

and the mass fraction 'f_i' of species i is given by

$$f_i = \frac{W_i}{\rho}$$

If X_i is the mole fraction of species i at the point, then

$$f_i = X_i M_i / \bar{M}$$

where $\bar{M}$ is the mean molecular weight of all species at the point.

Since the various forms of concentration are defined solely as quantities, concentration is a scalar variable.

Flux

The basic flux variable of a species i is the vector which defines the number of moles or grams of the species passing through unit area of the flame per unit time as viewed by a stationary observer.

The species mass flux is defined[30] by

$$g_i = N_i M_i (v + V_i)$$

for a one-dimensional flame

where v = the mass average velocity

V_i = the diffusion velocity of species i created by a concentration gradient.

The species mass flux fraction G_i is defined by:

$$G_i = \frac{N_i M_i (v + V_i)}{\rho v}$$

$$G_i = f_i \left(1 + \frac{V_i}{v}\right)$$

$$= \frac{X_i M_i}{\bar{M}} \left(1 + \frac{V_i}{v}\right)$$

In the absence of a concentration gradient $V_i = 0$ and $G_i = f_i$.

The diffusion velocity V_i in one-dimensional form for a species i present in an excess of carrier gas j is given by[30]

$$V_i = -N \frac{D_{ij}}{N_i} \frac{d}{dz} \left(\frac{N_i}{N}\right)$$

$$= -\frac{D_{ij}}{x_i} \frac{dX_i}{dz}$$

where N = the total number of moles present per unit volume at the plane.

D_{ij} = the binary diffusion coefficient for the species i in the excess carrier gas j. (D_{ij} is dependent on temperature.)

z = the height above the burner surface.

Thus $$G_i = \frac{X_i M_i}{\bar{M}} \left(1 + \frac{V_i}{v}\right)$$

or $$Gi = \frac{X_i M_i}{\bar{M}} \left(1 - \frac{D_{ij}}{vX_i} \frac{dX_i}{dz}\right)$$

This equation shows clearly the effect of a changing concentration gradient on the flux fraction of species i. In a region of increasing concentration $\frac{dX_i}{dz}$ is positive. Therefore $G_i < F_i$, an effect caused by the species flowing against the concentration gradient.

In a region of zero concentration gradient $\frac{dX_i}{dz} = 0$ and $G_i = f_i$

$$(G_i)_{maximum} = (f_i)_{maximum}$$

and $$(G_i)_{minimum} = (f_i)_{minimum}$$

In a region of decreasing concentration gradient $\frac{dX_i}{dz}$ is negative and thus $G_i > f_i$.

APPENDIX III.

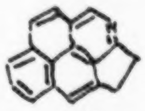
Hitherto Unidentified Polycyclic Aromatic Hydrocarbons Found in Flame Soots

I B. B. Chakraborty and R. Long[a] reported an unknown " derivative of pyrene" isolated from soot. This led to an exchange of letters between R. S. Thomas and J. L. Monkman[b.] and the above authors; Thomas and Monkman suggested it was a methyl pyrene, but as methyl pyrenes had already been identified as corresponding to an earlier peak in the gas chromatogram, Chakraborty and Long[b.] suggested that the unknown pyrene derivative they had found was of higher molecular weight than the methyl pyrenes.

L. Wallcave[c.] then reported an apparently identical compound which he had isolated from a coal tar pitch. The u. v. absorption spectrum of this substance had the seemingly characteristic peaks at 378 and 358 mμ reported by Chakraborty and Long.

Earlier M. J. Lyons[d.] had separated, interalia, by adsorption chromatography, a compound in a gasoline soot sample, in a diesel soot sample and in a general atmospheric soot sample, which gave spectral maxima, as follows, 376. (368), 355, 338, 324, 310, 291, 278 and which he designated "orange compound (pyrene derivative?)"

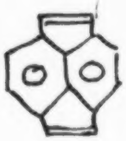
The u. v. spectrum of the "derivative of pyrene" reported by Chakraborty and Long shows several of these absorption maxima and is presumably the same compound. Based on his u. v. spectrum, on the chromatographic behaviour, and especially on the molecular weight as determined by mass spectrometry (228), Wallcave[c.] proposed that the compound in question was Cyclopenta (c, d) pyrene (or acepyrene).



228

II During the present work, in extraction filter products, B. D. Crittenden (Ph.D. thesis 1972) found a gas chromatographic peak, the mass spectrum of which showed two principal peaks at m/e values of 168 and 176 respectively (at 70 e. v.)

Since neither the methylbiphenyls nor biphenyl methane (molecular weight = 168) have a peak at m/e = 176 in their fragmentation mass spectra it was assumed that the gas chromatographic peak was due, at least in part, to a polycyclic aromatic hydrocarbon of molecular weight 176 and it was suggested that this might well be:-

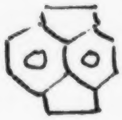


$C_{14}H_8$

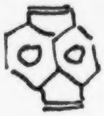
176

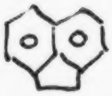
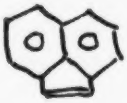
Rather strangely, K. H. Homann and H. Gg. Wagner[e.] in their study of rich premixed flat flames report the concentration change of only one, polycyclic aromatic hydrocarbon throughout their flame. This, a species with molecular mass 176 and having the formula $C_{14}H_8$, was said to be of medium concentration relatively to the others. They did not comment on its structure. A species, molecular weight (by mass spectrometry) of 176, was also found by E. E. Tompkins and R. Long[f.] in rich pre-mixed acetylene - oxygen flames.

The compound above appears never to have been isolated or synthesised. In 1952 A. G. Anderson Jr. and R. H. Wade[g] reported the synthesis of 'pyracene' or 1.2 -.dihydrocyclopenta (f, g) acenaphthene, and mentioned that an attempt was in progress to introduce a double bond



into each of the peri-rings in pyracene to form 'pyracylene'.



Acenaphthene  is a main constituent of coal tar and can easily be dehydrogenated to acenaphthylene 

However, the analogous compounds 'pyracene' and'pyracylene' have not been isolated or identified in coal tar on any fraction of coal tar.

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a.	B. B. Chakraborty and R. Long	Environ. Sci. Technol. I, 828, (1967)
b.	R. S. Thomas, and J. L. Monkman	ibid 2, 217 (1968)
b.	B. B. Chakraborty and R. Long	ibid 2, 217 (1968)
c.	L. Wallcave	ibid 3, 948 (1969)
d.	M. J. Lyons	Symposium, 'Analysis of Carcinogenic Air Pollutants' Aug. 1962. Nat. Cancer Inst. Monograph No. 9. U.S. Dept. of Health, Education & Welfare (1962).
e.	R. H. Homann and H. Gg. Wagner	Eleventh Symposium (International) on Combustion. The Combustion Institute, 1967 p. 371.
f.	E. E. Tompkins and R. Long	Twelfth Symposium on Combustion. 1969 p. 625
g.	A. G. Anderson Jr. and R. H. Wade	J. Amer. Chem. Soc. 74, 2274, (1952)